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1 Messinian carbonate-rich beds of the Tertiary Piedmont Basin (NW Italy): microbially-mediated  
2 products straddling the onset of the salinity crisis

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24 ABSTRACT

25 The seven Messinian microbial carbonate-rich layers cropping out in the Pollenzo section (Tertiary  
26 Piedmont Basin, NW Italy) are interbedded with a precession-related cyclic succession composed  
27 of euxinic shale/marl couplets and straddle the onset of the Messinian salinity crisis (MSC). A sharp  
28 change of sedimentological, compositional and geochemical characteristics was observed from the  
29 onset of the MSC onward, suggesting strong differences in the mechanisms responsible for  
30 carbonate precipitation. Pre-MSC beds are mainly composed of dolomite and are interpreted as the  
31 product of early diagenesis, formed by bacterial sulphate reduction in the shallow subsurface along  
32 the sulphate-methane interface. Dolomite precipitation was temporarily enhanced by an upward flux  
33 of methane-rich fluids, possibly sourced by gas hydrate destabilisation. Conversely, from the onset  
34 of the MSC onward, carbonate beds are thinly laminated and show abundant filaments interpreted  
35 as *Beggiatoa*-like bacteria, while calcite (and aragonite) are the dominant authigenic phases. These  
36 beds are interpreted as microbialites, resulting from the lithification of chemotrophic bacterial mats  
37 dominated by sulphide-oxidizing bacteria. The carbonate necessary for their preservation was  
38 provided by bacterial sulphate reduction. These microbialites, that appear as the deeper water  
39 counterpart of bottom-grown selenite layers deposited in the marginal part of the basin, formed on  
40 an anoxic sea bottom under a density stratified water column. The high sulphate concentration in  
41 the pore waters, related to the presence of concentrated brines and to the regeneration of sulphate by  
42 sulphide-oxidizing bacteria, is considered as the driving factor controlling the mineralogical change  
43 from dolomite to calcite and aragonite. Finally, the sharp shift toward negative  $\delta^{18}\text{O}$  values of  
44 carbonates, observed from the onset of the MSC onward, was probably related to fractionation  
45 processes operated by sulphate-reducing bacterial communities in the pore waters. This suggests  
46 that care must be taken, when dealing with microbial carbonates, in the interpretation of the oxygen  
47 isotope values in term of fluctuating salinity condition of the water mass. In conclusion, this study  
48 suggests that the onset of the MSC had a strong impact on microbial populations governing

49 carbonate precipitation, in a sector of the basin dominated by depositional conditions not suitable  
50 for gypsum precipitation.

51

52 *Key words:* bacterial sulphate reduction, bacterial sulphide oxidation, Messinian salinity crisis,  
53 microbial mats, Tertiary Piedmont Basin.

54

## 55 **1. Introduction**

56

57 Studies of modern environments and culture experiments have shown that microbially-  
58 induced carbonate precipitation is a common process active in various types of marine sediments  
59 (*e.g.* Irwin et al., 1977; Vasconcelos et al., 1995; Wright and Oren, 2005). In particular, sulphate-  
60 reducing bacteria are considered to play a fundamental role in triggering the precipitation of  
61 different carbonate minerals (calcite, aragonite, dolomite) in a wide range of organic-rich sediments  
62 from peritidal microbial mats (*e.g.* Baumgartner et al., 2006, Dupraz et al., 2009) to anoxic deep sea  
63 sediments (*e.g.* Meister et al. 2008). A prolonged and intense activity of the degradation of organic  
64 matter by sulphate-reducing bacteria can lead to the formation of lithified layers and masses,  
65 commonly referred to as microbialites. However, other prokaryotes are also thought to be related to  
66 carbonate precipitation and sediment lithification, including methanogenic archaea, anaerobic  
67 methane oxidizing communities, and cyanobacteria (see Wright and Oren 2005 and references  
68 therein). The correct identification of the prokaryotes involved in the formation of diagenetic  
69 carbonate bodies can provide fundamental information on the environmental conditions governing  
70 carbonate precipitation both at the sea bottom and in the shallow subsurface.

71 Microbial carbonate rocks are a common component of the Messinian salinity crisis (MSC)  
72 stratigraphic record. They have been mainly reported from: 1) the Terminal Carbonate Complex  
73 (Esteban, 1979), a syn- to post-evaporitic unit found in the western Mediterranean basins (*e.g.*  
74 Riding et al., 1998; Braga et al., 2006; Roveri et al., 2009) that is mostly composed of large

75 thrombolite and stromatolite domes (Feldmann and Mc Kenzie, 1997; Arenas and Pomar, 2010); 2)  
76 the Calcare di Base, a composite unit found in Sicily and Calabria below the gypsum or passing  
77 laterally into it (Decima et al., 1988; Garcia-Veigas et al., 1995; Oliveri et al., 2010). As  
78 summarised by Manzi et al. (2011), the Calcare di Base was interpreted as a chemical precipitate  
79 from concentrated brines immediately prior to evaporite deposition (Schreiber and Friedman, 1976;  
80 Decima et al., 1988) and/or as a microbial product formed in a restricted basin (Bellanca et al.,  
81 2001; Blanc-Valleron et. al., 2002). In particular, beds of carbonate “stromatolites” were reported  
82 (Oliveri et al., 2010) and interpreted as the record of progressively shallower, more restricted and  
83 hypersaline conditions, favouring the development of microbial communities at the sea floor  
84 immediately prior to the onset of gypsum deposition (*e.g.* Rouchy and Caruso, 2006). Wide salinity  
85 fluctuations and sharp dilution events of the brines have also been highlighted (Guido et al., 2007).  
86 A complex diagenetic evolution, including microbial sulphate reduction coupled to the oxidation of  
87 biogenic methane, was also proposed (Ziegenbalg et al., 2010, 2012). Similar beds were described  
88 below the gypsum from other Mediterranean localities such as the Vena del Gesso basin (Vai and  
89 Ricci Lucchi, 1977; Manzi et al., 2011) and Cyprus, where these features have been referred to as  
90 stromatolites and considered to record basin shallowing and restriction (Rouchy and Monty, 1981;  
91 Krijgsman et al., 2002; Orszag-Sperber et al., 2009).

92         A recent revisitation of the Calcare di Base in Sicily, Calabria and northern Apennines  
93 (Manzi et al., 2011) showed that this unit actually consists of several types of carbonates formed in  
94 different setting and during different stages of the Messinian salinity crisis. In particular, the unit  
95 includes three types of carbonates: a) thin dolostone beds interbedded to tripolaceous facies,  
96 representing the deep water equivalent of primary gypsum deposited in marginal basins during the  
97 first MSC step (type 2); b) clastic bodies deposited during the second MSC stage (type 3); c) late  
98 diagenetic products after original resedimented gypsum layers (type 1).

99         Thin carbonate beds are also known from the Piedmont succession, just below the gypsum  
100 (Sturani, 1973). In previous studies (Sturani, 1976) these beds, that abruptly overlie lower

101 Messinian deep water marls, were interpreted as the record of a dramatic sea level fall (of the order  
102 of 200-500 m) at the onset of the MSC. This interpretation was based on the presence of a variety of  
103 features thought to indicate deposition in very shallow waters and subaerial exposure (stromatolitic  
104 lamination, desiccation and expansion cracks, calcite pseudomorphs after gypsum crystals).  
105 However, a recent revisitation of the MSC record of the southern margin of the Piedmont Basin  
106 (Dela Pierre et al., 2011) suggested that these carbonate beds actually straddle the onset of the MSC  
107 and that part of them are the lateral deep-water counterpart of the lowermost gypsum layers  
108 deposited in the shallow marginal part of the basin, hence corresponding to the type 2 Calcare di  
109 Base (*sensu* Manzi et al., 2011, see above ) of the Sicilian succession.

110 In this paper we present the results of an integrated sedimentological, petrographical and  
111 geochemical study of Messinian carbonate beds, from the Pollenzo section. The results offer the  
112 opportunity to discuss the impact that the environmental changes related to the onset of the MSC  
113 had on microbial populations governing carbonate precipitation, in a sector of the basin dominated  
114 by depositional conditions not suitable for gypsum precipitation.

115

## 116 **2. The Messinian salinity crisis**

117

118 The MSC affected the Mediterranean basin between 5.96 and 5.33 Ma and resulted in the  
119 deposition of huge volumes of evaporites that are presently preserved both at the basin margins and  
120 in deep basinal areas, where they are buried below the abyssal plains of the Western and Eastern  
121 Mediterranean sea (*e.g.* Rouchy and Caruso, 2006). After the formulation of the desiccated deep  
122 basin model (Hsü et al., 1973; Cita et al., 1978), the nature and timing of the MSC events still  
123 remain the object of a lively scientific debate, mainly because a detailed correlation between the  
124 marginal sub-basins, that provide most of the outcropping successions (*e.g.* Clauzon et al., 1996;  
125 Krijgsman et al., 1999; Rouchy and Caruso, 2006; Manzi et al., 2007; Roveri et al., 2008; Lugli et  
126 al., 2010) and the deep basins, whose buried sedimentary record was analysed by seismic profiles,

127 is still lacking (Ryan, 1976; Bertoni and Cartwright, 2007; Lofi et al., 2011). Recently, a MSC  
128 evolutionary model has been proposed (CIESM, 2008). This model derives from the two step  
129 scenario of Clauzon et al. (1996) and envisages three MSC stages. During the first one (5.96-5.60  
130 Ma) primary evaporites were deposited only in shallow, silled, peripheral basins (Primary Lower  
131 Gypsum unit; Roveri et al., 2008). Carbonate microbialites are often reported below these deposits  
132 (*e.g.* Rouchy and Monty, 1981; Rouchy and Caruso, 2006). Conversely, in deep basinal setting,  
133 only euxinic shales and dolomite-rich beds (the type 2 Calcare di Base of Manzi et al., 2011) were  
134 deposited during this stage. The absence of gypsum and the concomitant formation of dolomite  
135 seem related to anoxic conditions, responsible for the decrease of the dissolved sulphate content via  
136 organic matter degradation by bacterial sulphate reduction (De Lange and Krijgsman, 2010).

137       During the second MSC stage (5.60-5.55 Ma) the marginal basins underwent subaerial  
138 exposure and erosion as evidenced by an erosional surface, referred to as the Messinian erosional  
139 surface (Lofi et al., 2011). This surface can be traced basinward in a correlative conformity placed  
140 at the base of thick accumulations of chaotic and resedimented evaporites, the Resedimented Lower  
141 Gypsum unit (Roveri et al., 2008).

142       During the third stage (5.55-5.33 Ma) a rapid transition to environments characterised by  
143 fluctuating salinity conditions is recorded by deposition of evaporites (Upper Evaporites) and clastic  
144 sediments containing brackish to fresh water fossil assemblages. The reestablishment of fully  
145 marine conditions at 5.33 Ma (Zanclean) marks the end of the salinity crisis.

146

### 147 **3. Geologic and stratigraphic setting**

148

149       The Tertiary Piedmont Basin (Figs. 1A, B) is filled with Upper Eocene to Messinian  
150 sediments deposited unconformably on a wedge of Alpine, Ligurian and Adria basement units  
151 juxtaposed in response to the collision between the Europe and Adria plates (*e.g.* Mosca et al.,  
152 2009; Rossi et al., 2009). Messinian strata were deposited in a wide wedge top basin (Figs. 1B, 2A),



153 bounded to the north by the more external Apennine thrusts (Rossi et al., 2009; Dela Pierre et al.,  
154 2011). The shallow marginal zones are presently exposed in the northern (Torino Hill and  
155 Monferrato) and southern (Langhe) sectors of the Piedmont Basin, whereas the depocentral zones  
156 are buried below Pliocene and Quaternary sediments (Savigliano and Alessandria basins) (Fig.1A).

157         The succession begins with outer shelf to slope muddy sediments referred to as the  
158 Sant'Agata Fossili Marls (Tortonian-lower Messinian) that record progressively more restricted  
159 conditions heralding the onset of the MSC (Sturani and Sampò, 1973). This unit displays a  
160 precession-related cyclic stacking pattern, evidenced by the rhythmic repetition of euxinic  
161 shale/marl couplets (Lozar et al., 2010), and is followed at basin margin by the Primary Lower  
162 Gypsum unit (Fig. 2A). The latter shows the same precession-driven lithologic cyclicity,  
163 represented by shale/gypsum couplets (Dela Pierre et al., 2011). No *in situ* primary evaporites are  
164 documented in the depocentral zones, but seismic data show that their time equivalent sediments are  
165 represented by shales (Irace et al., 2010).

166         The transition between the shallow marginal area and the buried depocentre is exposed on  
167 the southern sector of the Piedmont Basin (Alba region) and was reconstructed in detail along a  
168 SW-NE transect (Dela Pierre et al., 2011) (Fig. 2B). On the basin margins, six Primary Lower  
169 Gypsum cycles were recognised, composed of bottom grown-selenite layers; the sixth bed  
170 represents a distinct marker bed referred to as the Sturani key-bed (Dela Pierre et al., 2011). Moving  
171 towards the NE (*i.e.* towards the depocentral zone), only two gypsum beds are present below this  
172 marker bed. In the Pollenzo section they overlie a cyclic succession of euxinic shales, marls and  
173 carbonate-rich beds (the object of this study), belonging from the lithostratigraphic point of view to  
174 the Sant'Agata Fossili Marls (Fig. 2B). Due to their position with respect to the Sturani key-bed, the  
175 uppermost three cycles must be considered as the deeper water equivalent of the lower cycles of the  
176 Primary Lower Gypsum unit deposited in marginal setting (Dela Pierre et al., 2011). This  
177 correlation is confirmed by bio-magnetostratigraphic data, indicating that the onset of the MSC

178 should be placed at Pollenzo three cycles below the first gypsum bed, in correspondence of the peak  
179 abundance of the calcareous nannofossil *Sphenolithus abies* (Lozar et al., 2010).

180 The Primary Lower Gypsum unit is followed by resedimented and chaotic evaporites (Valle  
181 Versa Chaotic Complex, Dela Pierre et al., 2007), that are considered to be equivalents of the  
182 Resedimented Lower Gypsum unit (Fig. 2B) deposited during the second MSC stage (5.60-5.55  
183 Ma). This latter unit is finally followed by fluvio-deltaic and lacustrine deposits (Cassano Spinola  
184 Conglomerates) recording the third MSC stage (5.55-5.33 Ma), in turn overlain by Zanclean marine  
185 clays (Argille Azzurre Formation).

186

### 187 3.1 The Pollenzo section

188

189 In this section, located along the Tanaro River, a complete Messinian succession,  
190 comprising the Sant'Agata Fossili Marls, the Primary Lower Gypsum, the Resedimented Lower  
191 Gypsum units and the Cassano Spinola Conglomerates, is exposed (Fig. 3). Only the Sant'Agata  
192 Fossili Marls, in which the studied carbonate beds are hosted, will be described below. For the  
193 chrono-biostratigraphic data of this unit and for the description of the overlying succession, the  
194 reader is referred to Lozar et al. (2010) and Dela Pierre et al. (2011).

195 The Sant'Agata Fossili Marls consist of muddy marine sediments characterised by a  
196 distinctive precession-driven cyclicity, given by the alternation of euxinic shale/marl couplets,  
197 forming up to 3 m-thick cycles (Dela Pierre et al., 2011). A 80 m-thick slumped interval divides the  
198 section into two portions (Fig. 3). The lower portion, below the slump, consists of seven cycles; in  
199 the upper portion, above the slump, the lithologic cyclicity is enhanced by the regular repetition of  
200 carbonate-rich beds easily distinguishable for their whitish colour (Fig. 4). Seven cycles (Pm1-Pm7)  
201 with an average thickness of 3 metres were recognised, each one including a distinct carbonate bed.  
202 The integration of physical-stratigraphic (position with respect to the Sturani key-bed) and  
203 biostratigraphic data (peak abundance of the calcareous nannofossil *S. abies*), demonstrated that the

onset of the MSC must be placed at the base of cycle Pm5 (Lozar et al., 2010; Dela Pierre et al. 2011). Hence four pre-MSC cycles (Pm1-Pm4) are present, followed by three MSC cycles (Pm5-Pm7) that correspond to the lowermost Primary Lower Gypsum cycles recognised in the marginal part of the basin (Fig. 3).

Each pre-MSC cycles is composed of a basal layer of laminated euxinic shale, transitionally followed by a calcareous marly bed that hosts a dm-thick carbonate-rich bed. The strong impoverishment of foraminiferal assemblages, that include only rare stress tolerant planktic (*Turborotalita quinqueloba* and *T. multiloba*) and benthic taxa (*Bolivina dentellata* and *Bulimina echinata*), suggests the establishment of restricted conditions, a severe stratification of the water column and the impoverishment in dissolved oxygen of bottom waters (Lozar et al., 2010). The MSC cycles show analogous lithologic characteristics, but no marls were observed in cycle Pm6; moreover the carbonate beds here show a laminated structure, not observed in the underlying ones (see below). An hemi-ellipsoidal convex-upward indurated body has been observed 50 cm above layer *e*, within cycle Pm6 (Fig.3). This feature was not reported in Dela Pierre et al. (2011) because completely submerged at that time by the Tanaro River. Foraminifers and calcareous nannofossils are extremely rare and disappear at the top of cycle Pm6, confirming the final disruption of the water column and the definitive establishment of anoxic bottom conditions. The upper carbonate bed (*g*, Figs. 3, 4) is overlain by the first gypsum-bearing cycle (Pg1, Fig. 3), that is composed of laminated muddy siltstones followed by a 1-m thick massive selenite bed; this cycle corresponds to the 4<sup>th</sup> cycle of the Primary Lower Gypsum unit (Dela Pierre et al., 2011).

224

#### 225 4. Methods

226

Field studies of the lithology and geometry of the carbonate beds, including the relationships with the host sediments, were carried out on the upper portion of the Sant'Agata Fossili Marls, above the slump. Both the carbonate beds and the unconsolidated host sediments were sampled for

230 petrographic and geochemical analyses. Twelve standard thin sections of the most representative  
231 samples were studied under the optical microscope and were further analysed for their fluorescence,  
232 using a Nikon microscope equipped with a B-2a filter block (illumination source with an excitation  
233 wave length of 450-490 nm) (Department of Plant Biology, Torino University). Scanning Electron  
234 Microscopy (SEM) analyses were performed on 30 slightly etched polished surfaces using a SEM  
235 Cambridge Instruments Stereoscan 360 equipped with an energy-dispersive EDS Oxford  
236 Instruments Link System microprobe (Department of Earth Sciences, Torino University).  
237 Semiquantitative analyses on the amount of the carbonate fraction and on its mineralogical  
238 composition (calcite and dolomite) were carried out on 40 samples (including both the carbonate-  
239 rich beds and the host sediments) at the Inductively Coupled Plasma-Optical Emission  
240 Spectroscopy (ICP-OES) laboratory (Department of Earth Sciences, Torino University), using an  
241 IRIS II Advantage/1000 (Thermo-Jarrel Ash Corp.). As a first step, 2000 mg of sample powder  
242 were stirred for 48 h in 200 ml of distilled water, in order to dissolve the (diagenetic) gypsum  
243 possibly present in the sediments. The filtered solution was analysed and the amount of sulphur was  
244 measured. Assuming that all the sulphur derived from dissolution of gypsum (pyrite or silicates are  
245 not dissolved in distilled water), a corresponding stoichiometric amount of  $\text{Ca}^{2+}$  was then subtracted  
246 from to the whole  $\text{Ca}^{2+}$  pool (obtained in the further step) in order to avoid an overestimation of the  
247 carbonates. As a second step, 200 mg of sample powder were processed in 10 ml of hot acetic acid  
248 for 12 h, in order to dissolve the carbonates but at the same time preserving the silicates. The  
249 filtered solution was analysed and the amount of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  was measured. The relative  
250 abundance of calcite and dolomite in the samples was calculated (after subtraction of the amount of  
251  $\text{Ca}^{2+}$  derived from gypsum, as mentioned above) assigning the total amount of  $\text{Mg}^{2+}$ , with the  
252 corresponding amount of  $\text{Ca}^{2+}$ , to stoichiometric dolomite; the remaining  $\text{Ca}^{2+}$  was assumed to  
253 derive from calcite and was used to calculate the abundance of stoichiometric calcite. EDS analyses  
254 performed on some samples confirmed the near stoichiometric composition of calcite (less than 1%

255 of  $\text{Mg}^{2+}$ ), and dolomite (51- 53  $\text{CaCO}_3$  mole%). The results of Inductively Coupled Plasma (ICP)  
256 analyses (Table 1) are expressed as mass percent on the whole sediment.

257 Bulk rock C and O stable isotope analyses were performed on 22 samples from both  
258 carbonate-rich beds and unlithified sediments at the ISO4 laboratory (Torino, Italy) and in the  
259 *MARUM* Stable Isotope Laboratory (Bremen, Germany). The carbonate fraction was analysed  
260 following the classical method (McCrea, 1950). The  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios of the  $\text{CO}_2$  were  
261 obtained using Finnigan MAT 251 and 252 mass spectrometers. For the carbonate-rich beds, both  
262 calcite and dolomite were measured, whereas in the unconsolidated sediments only calcite was  
263 analysed. The isotopic ratios are expressed as  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  per mil versus the PDB standard (Fig.  
264 3, Table 3); the analytical error is  $\pm 0.5\text{‰}$  and  $\pm 0.1\text{‰}$  for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , respectively.

265

## 266 **5. Results**

### 267 *5.1. Lithology*

268

#### 269 *5.1.1 Unconsolidated sediments*

270 In the host sediments, the carbonate content ranges from 10 to 41% and consists of both  
271 calcite and dolomite that are mixed in variable proportions (Table 1). The total carbonate ranges  
272 from 23 to 41% in the homogeneous marl and reaches the lowest values ( $<23\%$ ) in the laminated  
273 shale. As a general rule, pre-MSC sediments contain a higher calcite fraction, probably related to  
274 the higher content of skeletal grains (foraminifers and calcareous nannofossils), that are generally  
275 very rare or even absent in MSC sediments.

276

#### 277 *5.1.2 Pre-MSC carbonate-rich beds*

278 Pre-MSC beds (*a*, *b*, *c*, *d*) are dm- thick and are interbedded within the marly part of the  
279 lithologic cycles (Pm1 to Pm4, Fig. 3). The lower and upper contacts are transitional, except for bed  
280 *a* in which they are sharp (Fig. 5A). These beds are the product of local cementation of host

281 sediments and contain variable amounts of a silt-sized terrigenous fraction, mainly consisting of  
282 mica flakes. All beds are strongly bioturbated (Figs. 5B, C), suggesting deposition on an  
283 oxygenated sea bottom, and contain planktic and benthic foraminifers, and calcareous nannofossils.

284 The intergranular cement mostly consists of idiomorphic rhombohedral crystals of  
285 dolomite, ranging in size from 2 to 10  $\mu\text{m}$  (Fig. 5D). Calcite is also present, both of biogenic and  
286 diagenetic origin. The mixture is confirmed by data from ICP analyses (Tables 1 and 2); they show  
287 that in beds *a*, *b* and *d* dolomite represents 91.9, 68.0 and 83.3% of the total carbonate content  
288 (76.1, 63.1 and 45.1% respectively over the bulk composition). Conversely in bed *c* the total  
289 carbonate fraction (48.2%) consists of similar proportions of calcite and dolomite (51.7 and 48.3%,  
290 respectively) (Fig. 3, Table 2). Pyrite framboids, up to 10  $\mu\text{m}$  across, are very common in all beds  
291 (Fig. 5E).

292

### 293 5.1.3 MSC carbonate-rich beds

294 Beds deposited during the salinity crisis are about 20 cm-thick and show transitional  
295 contacts with the host sediments (Fig. 6A). Bed *e* is located at the top of the marly interval and  
296 contains mm-sized intraclasts, floating in a clotted micrite matrix containing rare foraminifers. A  
297 remarkable feature is the presence of contractional cracks developed around the clasts  
298 (circumgranular cracks) (Fig. 6B). Beds *f* and *g* show different features, because they are not  
299 bioturbated and display a well-developed lamination. Bed *f* lies in strongly laminated shales (no  
300 marl was observed in cycle Pm6) and shows a lamination marked by the alternation of mm-thick  
301 whitish and grey wrinkled laminae (Fig. 6C). The formers are composed of clotted micrite, contain  
302 abundant pyrite framboids and are crossed by a network of mm-wide contractional cracks, running  
303 perpendicular to the lamina surfaces, that are empty or filled with late diagenetic gypsum (Fig. 6D).  
304 These laminae contain abundant fish vertebrae and scales. The grey laminae are richer in  
305 terrigenous material, mostly represented by clay particles and mica flakes (Fig. 6D). At the  
306 boundary between the two types of laminae, cracks were commonly observed. Micrite laminae

307 exhibit a stronger epifluorescence than the terrigenous ones, suggesting a higher content in organic  
308 matter (Fig. 6E). Moreover, epifluorescence microscopy permits the recognition of filaments, up to  
309 100  $\mu\text{m}$  across and more than 300  $\mu\text{m}$  long, showing different fluorescence shades (Fig. 6E). Bed *g*  
310 is similar to bed *f*, except it is made up of more wrinkled and thinner laminae (less than 1 mm).  
311 Pyrite framboids are abundant and are frequently grouped together to mimic filaments about 100  
312  $\mu\text{m}$  across and up to 800  $\mu\text{m}$  long (Figs. 7A, C). Epifluorescence observations reveal that filaments  
313 show a stronger fluorescence than the enclosing matrix (Fig. 7D). The same features, despite less  
314 abundant, were observed in bed *f*.

315 Unlike the pre-MSC beds, the carbonate fraction of the salinity crisis layers is dominated by  
316 calcite whereas dolomite is subordinate; frequently micron-sized calcite crystals show a globular  
317 shape with a central hollow, suggesting a possible microbial origin (Cavagna et al., 1999). This type  
318 of crystals (Fig. 7B) was observed also within the filaments, together with abundant pyrite  
319 framboids. Remarkably, no terrigenous grains, abundant in the enclosing matrix, were observed  
320 within the filaments. The predominance of calcite over dolomite is confirmed by ICP analyses; in  
321 beds *e*, *f* and *g* calcite is 80.2, 84.1 and 94.8% of the total carbonate content (84.6, 69.1 and 59.0%,  
322 respectively) (Fig.3, Table 2).

323

#### 324 5.1.4 The hemi-ellipsoidal body

325 The hemi-ellipsoidal cemented body observed within cycle Pm6 is 1.70 metres by 1 metre in  
326 size and shows transitional lateral contacts with the host laminated shale (Fig. 8A). Its most  
327 remarkable feature is the wrinkled lamination (Fig. 8B), given by the alternation of submillimetric  
328 whitish and grey laminae, that strongly resembles the structure described as the “stromatolites” of the  
329 Sicilian Calcare di Base (Oliveri et al., 2010). The whitish laminae are composed of filaments, 150  
330  $\mu\text{m}$  across and up to few millimetres long (Fig. 8C), that are irregularly oriented or with their  
331 maximum dimension parallel to the lamina surface. The filaments are made of clotted micrite,  
332 composed of micron-sized strongly epifluorescent calcite crystals (Figs. 8D, F). They are



commonly curved and are surrounded by fringing aragonite (Figs. 8E, F). No terrigenous grains were observed in the filaments, as in beds *f* and *g*. Grey laminae are richer in terrigenous grains, are laterally discontinuous and seal the undulating microtopography formed by the former white laminar structures. Moreover, mm-sized *fenestrae*, likely resulting from dissolution of former gypsum crystals, are present. Pyrite framboids, up to 20  $\mu\text{m}$  across, are very common in both types of laminae and frequently cap acicular aragonite crystals (Fig. 9).

## 5.2. Stable isotope data

### 5.2.1 Unconsolidated sediments

In both pre-MSC and MSC cycles, the  $\delta^{13}\text{C}$  values are around zero (Fig. 3, Table 3), suggesting carbonate precipitation from a fluid in isotopic equilibrium with sea water. The weak  $^{13}\text{C}$  depletion observed in some samples from cycles Pm1 ( $\delta^{13}\text{C} = -6.5\text{‰}$ ), Pm6 ( $\delta^{13}\text{C} = -5\text{‰}$ ) and Pm7 ( $\delta^{13}\text{C} = -4.7\text{‰}$ ) points to the contribution of diagenetic carbon from decaying organic matter. All samples are characterised by low  $\delta^{18}\text{O}$  values, with a general trend towards more negative values in the MSC sediments (cycle Pm5-Pm7). The interpretation of these negative  $\delta^{18}\text{O}$  values is not straightforward, because the analysed carbonate fraction is sparse (<23%) and the resultant values can reflect the contribution of different carbonate pools (detrital, skeletal, diagenetic), mixed in unknown ratios. However, these low values, commonly interpreted as the result of an overall “freshening” of the water mass under the increased influx of fresh water (*e.g.* Blanc-Valleron et al., 2002), may reflect complex microbial fractionation processes on the oxygen pool (see paragraph 6.2.2).

### 5.2.2 Pre-MSC carbonate-rich beds



357 A significant  $^{13}\text{C}$  depletion was observed for both dolomite and calcite in beds *a* and *b*  
358 ( $\delta^{13}\text{C}_{\text{dol}} = -19.8$  and  $-21\text{‰}$ ;  $\delta^{13}\text{C}_{\text{cal}} = -16.7$  and  $-14.5\text{‰}$ , respectively). In the upper two pre-MSC  
359 beds (*c* and *d*) less negative values were instead measured for both minerals ( $-4.4$  and  $-5.2\text{‰}$  for  
360 dolomite;  $-9.2$  and  $-5.7\text{‰}$  for calcite, respectively). Positive  $\delta^{18}\text{O}_{\text{dol}}$  values were observed in all  
361 pre-MSC beds (Fig. 3, Table 3): the stronger  $^{18}\text{O}$  enrichment was measured in beds *a* ( $\delta^{18}\text{O}_{\text{dol}} =$   
362  $+7\text{‰}$ ) and *b* ( $\delta^{18}\text{O}_{\text{dol}} = +6.9\text{‰}$ ), whereas in beds *c* and *d* lower values were found ( $\delta^{18}\text{O}_{\text{dol}} = +1.3$   
363 and  $+3.6\text{‰}$ , respectively). More negative values were observed for calcite. In beds *a* and *b* the  
364  $\delta^{18}\text{O}_{\text{cal}}$  is  $+5.7$  and  $-1.0\text{‰}$ , respectively, whereas in beds *c* and *d* it is  $-3.9$  and  $-1.5\text{‰}$  (Fig. 3,  
365 Table 3).

366

### 367 5.2.3 MSC carbonate-rich beds

368 In the salinity crisis beds, the  $\delta^{13}\text{C}$  values of both dolomite and calcite are moderately  
369 negative (from  $-5$  to  $-3.9\text{‰}$  for dolomite and from  $-7.9$  to  $-6.7\text{‰}$  for calcite). A stronger  $^{13}\text{C}$   
370 depletion was measured for the calcite of the hemi-ellipsoidal body (cycle Pm6), with values around  
371  $-8.5\text{‰}$ . For what concerns the  $\delta^{18}\text{O}$ , a remarkable shift towards negative values was observed. The  
372  $\delta^{18}\text{O}_{\text{dol}}$  values range from  $-6.1$  to  $-4.9\text{‰}$  whereas the  $\delta^{18}\text{O}_{\text{cal}}$  are more negative (from  $-6.5$  to  $-$   
373  $8.8\text{‰}$ ). The hemiellipsoidal body yielded  $\delta^{18}\text{O}_{\text{cal}}$  values as low as  $-7.7\text{‰}$ .

374

375

## 376 6. Discussion

377

### 378 6.1. Pre-MSC beds: early diagenetic products from the shallow subsurface

379

380 In pre-MSC beds, the authigenic carbonate fraction is dominated by dolomite, mixed with  
381 variable amounts of calcite whose specific origin (detrital, skeletal and/or diagenetic) could not be

determined. The beds formed in strongly bioturbated sediments, deposited on an oxygenated sea bottom. The absence of traces of exposure of the indurated sediments at sea floor (*e.g.* firm ground burrows, borings) suggests that carbonate precipitation occurred within the sedimentary column. On the other hand the high authigenic carbonate content (45-76%) indicates that these beds formed in the shallow subsurface, within still porous mud not yet affected by mechanical compaction.

Studies of modern environments and culture experiments have shown that dolomite precipitation in the subsurface is induced by the metabolic activity of sulphate-reducing bacteria that, by degrading organic matter, consume sulphate ions and increase overall alkalinity thus overcoming the kinetic inhibition to dolomite precipitation (*e.g.* Baker and Kastner, 1981; Compton et al., 1988; Vasconcelos et al., 1995; Wright and Oren, 2005; Baumgartner et al., 2006; Meister et al., 2007; Wacey et al., 2008). In modern deep sea organic-carbon-rich hemipelagic sediments, bacterial sulphate reduction is controlled by the downward diffusion of sulphate from sea water (Compton, 1988; Wright and Oren, 2005). In these conditions, dolomite can precipitate from anoxic sulphate-free pore waters, at the lower boundary of the sulphate-reducing zone. In present-day open marine environments the depth of this surface, that corresponds to the sulphate-methane interface, ranges from few metres up to few tens of metres, depending on the porosity and on the content and type of organic matter (*e.g.* Borowski et al., 1999; Fossing et al., 2000; D'Hondt et al., 2002; Treude et al., 2005; Jørgensen and Kasten, 2006). Apart from carbonate, sulphate reduction provides hydrogen sulphide that subsequently can react with iron to form sulphide minerals (*e.g.* pyrite). Carbonate precipitation at the sulphate-methane interface is however quantitatively limited and commonly goes unnoticed in most sedimentary sequences (*e.g.* Raiswell and Fisher, 2004). In two cases it becomes significant and may give origin to well recognizable carbonate-cemented layers: 1) if large amounts of upward rising methane-rich fluids reach this geochemical interface; in this case abundant carbonate (calcite, aragonite and dolomite) can precipitate resulting in extensive cementation of the flushed sediments (*e.g.* Irwin et al., 1977; Raiswell, 1987; Raiswell and Fischer, 2000; Campbell, 2006; Ussler and Paull, 2008). Carbonate precipitation is induced by a consortium

408 of sulphate-reducing bacteria and methanotrophic archaea (Boetius et al., 2000), responsible for the  
409 anaerobic oxidation of methane; 2) if the sulphate-methane interface remains stationary within the  
410 sedimentary column for a prolonged time interval, resulting in focused dolomite precipitation; in  
411 this case, a distinct dolomite-rich bed can form even though the supply of methane-rich fluids from  
412 below is negligible (Meister et al., 2007, 2008).

413 The bed-parallel geometry of the Pollenzo pre-MSC beds suggests that dolomite  
414 precipitation occurred at a geochemical interface parallel to the sea bottom. In this regards the co-  
415 occurrence of authigenic carbonate and pyrite and isotopic data suggests that these beds may have  
416 formed at the sulphate-methane interface. In particular, the (moderately) negative  $\delta^{13}\text{C}$  values  
417 measured in diagenetic dolomite of the lower two beds (*a* and *b*) ( $\delta^{13}\text{C}$  around  $-20\text{‰}$ ), points to the  
418 contribution of anaerobic oxidation of methane in dolomite precipitation (Fig. 10A). The moderate  
419  $^{13}\text{C}$  depletion (compared to typical methane-derived carbonates in which  $\delta^{13}\text{C}$  values as low as  $-$   
420  $60\text{‰}$  are commonly measured; *e.g.* Peckmann and Thiel, 2004) may reflect the mixture of methane-  
421 derived carbon with other sources, such as heavier hydrocarbons (Roberts and Aharon, 1994),  
422 marine dissolved inorganic carbon or skeletal material of marine organisms, that are actually  
423 present in these beds (*e.g.* Peckmann and Thiel, 2004; Natalicchio et al., 2012). The same  
424 mechanism can explain the  $\delta^{13}\text{C}$  signature of calcite.

425 Conversely, the less negative  $\delta^{13}\text{C}$  values of beds *c* and *d* ( $\delta^{13}\text{C}$  around  $-5\text{‰}$ ) suggest that  
426 dolomite precipitation was induced by organoclastic bacterial sulphate reduction alone, as the  
427 upward methane flux ceased completely (Fig. 10B). These indurated layers likely developed along a  
428 temporarily fixed sulphate-methane interface that favoured focused dolomite precipitation. Sulphate  
429 reduction alone, however, was able to produce only a lesser amount of authigenic dolomite with  
430 respect to anaerobic oxidation of methane, as indicated by geochemical data and by the minor  
431 induration of these beds.

432 The oxygen isotope record of dolomite (the predominant carbonate mineral) reveals that  
433 beds *a* and *b* are significantly enriched in the heavy  $^{18}\text{O}$  isotope (Fig. 3, Table 3). Three mechanisms  
434 can explain such an enrichment:

435 a) evaporation of sea water (McKenzie et al., 1979). This mechanism, commonly invoked to  
436 explain the  $^{18}\text{O}$  enrichment of Messinian carbonates (*e.g.* Rouchy et al., 1998; Bellanca et al., 2001;  
437 Blanc-Valleron et al., 2002) should in our case be ruled out, because these beds formed before the  
438 onset of the MSC. Moreover, it strongly contrasts with the negative values of host sediments;

439 b) upward movement of deep fluids whose isotopic composition was modified by  
440 dehydration of smectite clay minerals (*e.g.* Dählmann and De Lange, 2003). The possible role  
441 played by this process can not be ruled out because of the lack of information on the source fluids  
442 and on clay mineralogy of underlying sediments;

443 c) flushing of sediments by methane-rich fluids sourced by gas hydrate destabilisation. This  
444 mechanism is consistent with the association of positive  $\delta^{18}\text{O}$  values with negative  $\delta^{13}\text{C}$  ones, as  
445 already suggested for lower Messinian dolomite layers and concretions found in the eastern part of  
446 the Piedmont Basin (Dela Pierre et al., 2010; Martire et al., 2010; Natalicchio et al., 2012), Spain  
447 and Northern Morocco (Pierre and Rouchy, 2004). Conversely, the lower oxygen values measured  
448 in beds *c* and *d*, that are coupled with slightly negative  $\delta^{13}\text{C}$  ones, suggest that the input of  $^{18}\text{O}$ -  
449 enriched fluids, ceased together with the demise of methane-rich fluids.

450 As already mentioned, the more negative  $\delta^{18}\text{O}_{\text{cal}}$  values probably reflect the mixing of  
451 authigenic and sedimentary calcite. Positive values were only observed in bed *a*, in which the scarce  
452 calcite content (8.1%) is likely diagenetic and cogenetic with dolomite.

453

## 454 6.2. MSC beds

455

456 A sharp change of sedimentological, compositional and geochemical characteristics is  
457 observed in the MSC beds. This change is shown by the following features that will be discussed

458 separately below: a) the presence of wrinkled laminae containing filament remains, and of  
459 contractional cracks; b) the sharp decrease of the dolomite content and the concomitant increase of  
460 the calcite (and aragonite) content; c) the negative  $\delta^{18}\text{O}$  values recorded both in calcite and  
461 dolomite. The carbon isotope data are instead comparable to those of the underlying pre-MSC beds  
462 and of the host sediments, testifying to the incorporation of light organic carbon in the authigenic  
463 phase.

464

465 *6.2.1. Wrinkled laminae, filaments and contractional cracks: vestiges of chemotrophic microbial*  
466 *mats?*

467 The submillimetric wrinkled lamination and the peloidal clotted microfabric of the micrite  
468 laminae, observed in beds *f* and *g* and in the hemi-ellipsoidal body of cycle Pm6, are typical  
469 features of carbonate microbialites, *i.e.* organo-sedimentary deposits formed by the activity of  
470 benthic microbial communities (Dupraz and Visscher, 2005; Dupraz et al., 2009; Oliveri et al.,  
471 2010). Compelling evidence of the involvement of microbial mats in the formation of laminated  
472 structure is given by the remains of microbial filaments, well recognizable in epifluorescence (Fig  
473 6E) that in beds *f* and *g* are underlined by a concentration of pyrite framboids (Figs.7C, D).  
474 Microbial filaments have been first observed in Messinian gypsum crystals (the so called *spaghetti-*  
475 *like* structures; Vai and Ricci Lucchi, 1977) and interpreted as remains of filamentous  
476 photosynthetic cyanobacteria (*e.g. Scytonema*) on the basis of size and internal structure (Rouchy  
477 and Monty, 1981; Panieri et al., 2010), thus providing evidence for shallow water (photic)  
478 depositional conditions (but see also the discussion about the relevance of these features for water  
479 depth determination in Lugli et al., 2010). Analogous features were then observed in carbonate  
480 deposits below the gypsum and were considered either as faecal pellets (Guido et al., 2007) or as  
481 cyanobacteria remains on the basis of their similarities with the *spaghetti* structures (Rouchy and  
482 Monty, 1981; Orszag-Sperber et al., 2009). Hence, also these carbonates were classically

483 interpreted as shallow water deposits recording stressed environmental conditions heralding the  
484 onset of the MSC.

485         The absence of terrigenous grains within the Pollenzo filaments allows to rule out their  
486 faecal origin. An alternative hypothesis is that these filaments represent remains of colourless  
487 sulphide-oxidizing bacteria like *Beggiatoa*, *Thiopluca* and *Thiotrix*. These giant bacteria, that can  
488 reach a diameter of 750  $\mu\text{m}$  and a length of several cm, obtain the energy necessary for their life  
489 from the oxidation of sulphide by using oxygen or nitrate as electron acceptors (Schulz and  
490 Jørgensen, 2001) and do not necessitate light as the driving energy source. In modern settings, they  
491 form dense microbial mats (known as chemotrophic-dominated mats) thriving at different water  
492 depth (from peritidal to bathyal settings), especially at sites where high concentration of sulphide is  
493 available at the sea bottom (*e.g.* Bailey et al., 2009) such as hydrothermal vents (*e.g.* Jannasch et al.,  
494 1989) and cold seeps (Larkin et al., 1994, Sahling et al., 2002; Teichert et al. 2005). However,  
495 sulphide-oxidizing bacteria are also known to form extensive felt-like mats where organic-rich  
496 sediments are exposed at the sea floor in contact with either oxic (Schulz et al., 1999) or oxygen-  
497 depleted waters, such as the continental shelf off Peru (Gallardo, 1977; Fossing et al., 1995) or the  
498 Danish Limfjorden (Mussmann et al. 2003). In these cases the bacteria use nitrate (and not oxygen)  
499 as electron acceptor for oxidizing sulphide to sulphate.

500         Though there are substantial similarities between the filamentous cyanobacteria and the  
501 sulphide-oxidizing bacteria and their distinction is difficult on morphology only, we propose that  
502 the Pollenzo filaments are remains of sulphide-oxidizing bacteria on the basis of the following  
503 elements: a) their diameter ( $>100\ \mu\text{m}$ ), that is close to that of living forms. On the contrary,  
504 cyanobacteria filaments rarely exceed 80  $\mu\text{m}$  (*e.g.* Schulz and Jørgensen, 2001); b) the curved shape  
505 of some filaments (Fig. 8E) consistent with the chemotactic behaviour of these prokaryotes that  
506 often change their direction in the search of optimal concentrations of oxygen or nitrate (*e.g.*  
507 Møeller et al., 1985); c) the concentration of pyrite framboids outlining the filament shape (beds *f*  
508 and *g*, Figs. 7C, D). Living sulphide-oxidizing bacteria host elemental sulphur globules within the

cytoplasm, that can be further preserved as sulphur-containing minerals associated to the filamentous body fossil (*e.g.* Bailey et al., 2009); d) the lack of any remain of shallow water macrobiota that should accompany photosynthetic mats. The only features that could suggest a shallow water origin for these laminated layers are the contractional cracks, either developed around clasts and nodules (circumgranular cracks, Fig. 6B) or placed parallel and perpendicular to the bedding (Fig. 6D). Similar features were previously interpreted as desiccation structures and hence considered as a compelling evidence of the subaerial exposure of the Piedmont basin at the onset of the MSC (Sturani, 1973). However, the geometry of crack, that are developed especially across the carbonate-rich laminae and thin out both in the under- and overlying terrigenous laminae, contrasts with an origin by subaerial exposure and desiccation. The microbial origin for the carbonates may provide an alternative explanation for the genesis of these cracks, that can be interpreted as the product of syneresis, related to the decay of bacterial extracellular polysaccharide substances (EPS) binding clay particles (*e.g.* Dewhurst et al., 1999; Hendry et al., 2006) in a subaqueous environment.

On this basis, beds *f* and *g* and the hemi-ellipsoidal body of cycle Pm6 are interpreted as the product of the lithification of chemotrophic microbial mats dominated by sulphide-oxidizing bacteria. Unlike their photosynthetic counterpart, chemotrophic mats are rarely preserved in the fossil record, because the metabolism of sulphide-oxidizing bacteria increases acidity and consequently induces carbonate dissolution rather than precipitation (*e.g.* Petrash et al. 2012). Their preservation can however take place if other biogeochemical processes trigger the rapid precipitation of authigenic carbonates necessary for the entombment of the delicate filaments before their complete decay. This may explain why putative fossil remains of sulphide-oxidizing bacteria are chiefly reported from ancient seep carbonate deposits, where anaerobic oxidation of vigorous methane fluxes induced extensive syndepositional carbonate precipitation (Peckmann et al., 2004). Described examples of filaments attributed to the genus *Beggiatoa* have been reported from cold seep deposits of the Miocene of Italy (Cavagna et al., 1999; Peckmann et al., 2004; Barbieri and



535 Cavalazzi, 2005) and the Oligocene of Poland (Bojanowski, 2007). Another example is the  
536 Messinian Calcare di Base of Sicily in which *Beggiatoa* filaments are entombed in a clotted  
537 peloidal dolomicrite resulting from bacterial sulphate reduction (Oliveri et al., 2010).

538         The slightly depleted  $\delta^{13}\text{C}$  values of the Pollenzo beds exclude a significant contribution of  
539 anaerobic oxidation of methane and suggest that the main process responsible for carbonate  
540 precipitation was degradation of organic matter via bacterial sulphate reduction. The characteristics  
541 of the MSC beds allow to envisage the following scenario (Figs. 11, 12): changed environmental  
542 conditions (anoxia of bottom waters, see below) favoured the shift of sulphate-reducing bacteria  
543 communities toward the sea bottom and their establishment immediately below it, where they could  
544 rely on abundant “fresh” organic matter; bottom anoxia actually inhibited aerobic oxidation of the  
545 organic remains reaching the sea bottom (Fig. 11). Along with carbonate precipitation, bacterial  
546 sulphate reduction provided an upward flux of hydrogen sulphide that sustained sulphide-oxidizing  
547 bacterial communities at the sea floor. Due to bottom anoxia, nitrate was used as electron acceptor  
548 by these prokaryotes for oxidizing sulphides to sulphates (Fig.12A). Intervals of higher sediment  
549 input and increase of continental runoff, recorded by the laminae richer in terrigenous grains,  
550 resulted in the aggradation of the sea bottom (Fig.12B). In these renewed conditions, microbial  
551 communities were forced to migrate upward and the sea bottom was covered by a “new” mat  
552 dominated by sulphide oxidizers. The availability of abundant and “fresh” organic matter increased  
553 the rate of sulphate reduction in the shallow subsurface, and resulted in the rapid precipitation of  
554 large amounts of carbonates preserving the previously formed mat (Fig. 12C). The repetition of  
555 these processes through time led to the formation of the laminated structure that characterizes these  
556 rocks. According to the proposed scenario, sulphide oxidation, that promoted acidity and carbonate  
557 dissolution, was hence spatially and temporally decoupled from the alkalinity generated by sulphate  
558 reduction inducing carbonate precipitation. EPS degradation prior to complete lithification was  
559 responsible for the opening of contractional cracks. These features are also observed in bed *e*,  
560 confirming the active role played by microbial activity in its formation.



561 The hemi-ellipsoidal body within cycle Pm6 differs from under-and overlying beds for its  
562 geometry and for the more varied authigenic carbonate composition, including aragonite. This  
563 feature likely developed above a local source of decomposing organic matter, able to sustain an  
564 intense activity of the same bacterial consortia described above, as observed today around whale  
565 falls (*e.g.* Treude et al., 2009) or sunken woods (*e.g.* Palacios et al., 2009). Enhanced bacterial  
566 activity was responsible for the formation of large amount of calcite, that was followed by  
567 precipitation of the aragonite fringes rimming the bacterial filaments.

568

569 *6.2.2 The change from dolomite to Ca-carbonates and the oxygen isotope composition of MSC*  
570 *beds*

571 The other points to be discussed are: a) the mineralogical change recorded from the MSC  
572 onset onward, evidenced by the sharp increase in the calcite content and by the appearance of  
573 aragonite in the hemi-ellipsoidal body; b) the negative  $\delta^{18}\text{O}$  values of the MSC carbonates.

574 Although still discussed (Sánchez-Román et al., 2009), the concentration of sulphate in the  
575 pore waters is a critical factor controlling the composition of bacterially-induced carbonate  
576 minerals. In particular, if the concentration of sulphate is high, dolomite is inhibited and other  
577 carbonates (aragonite, calcite, Mg-calcite,) do form (*e.g.* Baker and Kastner, 1981; Kastner, 1984;  
578 Wright and Oren, 2005). At Pollenzo, the main factor driving carbonate precipitation both in pre-  
579 MSC and in MSC layers was bacterial sulphate reduction. However in pre-MSC beds the sulphate  
580 in pore waters was exclusively supplied by normal salinity sea water and carbonate precipitation  
581 took place within the sedimentary column. Under these conditions, all sulphate was consumed by  
582 bacterial sulphate reduction and dolomite precipitation took place from sulphate-free pore waters  
583 along the sulphate-methane interface.

584 On the contrary, MSC beds and the hemi-ellipsoidal body formed at the sea bottom in  
585 contact with sulphate-enriched bottom waters, being these layers the lateral equivalents of bottom-  
586 grown selenite beds formed in the shallower part of the basin, some tens of kilometres apart.

587 Moreover, the sulphate pool was continuously replenished by sulphide oxidation in the  
588 chemotrophic microbial mats. As a consequence, sulphate could not be totally consumed, even in  
589 the presence of an intense bacterial sulphate reduction, and precipitation of Ca-carbonates (calcite,  
590 aragonite) was favoured. Minor amounts of dolomite, occupying the residual pore space formed  
591 only after sediment burial, when all sulphate was consumed. This last mechanism was also  
592 responsible for the minor amount of dolomite in the host sediments.

593 The shift towards more negative  $\delta^{18}\text{O}$  values observed in MSC carbonates ( $-6.5 < \delta^{18}\text{O}_{\text{cal}} < -$   
594  $8.8\text{‰}$  PDB;  $-4.9 < \delta^{18}\text{O}_{\text{dol}} < -6.1\text{‰}$  PDB) compared to the underlying pre-MSC ones remains a still  
595 unresolved question. Such  $^{18}\text{O}$  depletion is reported from carbonates just below the first evaporitic  
596 deposits in other Mediterranean basins (even if less severe than at Pollenzo) and is interpreted as the  
597 result of sharp dilution events pointing to the isolation of the basin(s) prior to the onset of gypsum  
598 deposition (e.g. Rouchy et al., 1998; Bellanca et al., 2001; Blanc-Valleron et al., 2002). This  
599 interpretation is hardly reconcilable with the Pollenzo beds, that are the lateral equivalents of  
600 gypsum. Alternative hypotheses have been proposed, that point to microbial sulphate consumption  
601 as a possible source of  $^{16}\text{O}$  enrichment in the microenvironments of carbonate precipitation (Sass et  
602 al., 1991). The effects of this process on oxygen isotopic ratios both of sulphate and water have  
603 been studied, since the seminal work of Lloyd (1968), with theoretical and experimental approaches  
604 (e.g. Fritz et al., 1989; Brunner et al., 2005; Wortmann et al., 2007) but several aspect remain  
605 unresolved and, citing Turchyn et al. (2010) “more work is needed”.

606

### 607 6.2.3 *The lateral equivalent of gypsum: microbialites reflecting chemotrophic activity*

608 Recent MSC palaeohydrological models (Krijgsman and Meijers, 2008), predict that during  
609 deposition of the Lower Evaporites, the onset of gypsum deposition led to severe density  
610 stratification of the Mediterranean water column that resulted in turn in a well mixed, upper water  
611 mass underlain by an oxygen-depleted deep water mass. Similar conditions likely existed in the  
612 Piedmont Basin during the first MSC stage and may explain why microbialites reflecting the

activity of chemotrophic prokaryotes are the lateral equivalent of bottom-grown selenite beds (Dela Pierre et al., 2011, Fig. 2B). According to field and theoretical models, anoxic sea bottoms would be unfavourable to gypsum formation and preservation, mainly because of low sulphate concentration related in turn to intense bacterial sulphate reduction (*e.g.* Babel, 2007; De Lange and Krijgsman, 2010). On the other hand, this last process produced large amounts of hydrogen sulphide favouring the development of dense chemotrophic microbial mats at the sea floor. Due to the low rate of terrigenous supply, the latter could colonize the sea bottom for a prolonged time interval before their final burial. This circumstance, along with an increased rate of bacterial-mediated carbonate precipitation, allowed the preservation of discrete recognizable beds in the geological record.

## 7. Conclusions

The carbonate-rich layers of the Pollenzo section straddle the onset of the MSC and provide a detailed record of the environmental changes related to this palaeocenographic event in a sector of the basin where depositional conditions were not suitable for gypsum formation. The integration of field and laboratory data permitted the recognition of the strong difference in the mechanisms responsible for carbonate precipitation before and after the salinity crisis onset.

Dolomite rich-beds actually formed only prior to the onset of the MSC; this interpretation is partially at odds with previous theoretical models (De Lange and Krijgsman, 2010), according to which dolostone layers are the lateral equivalents of the Primay Lower Gypsum beds formed during the first stage of the MSC. The Pollenzo pre-MSC beds are early diagenetic products formed within the sedimentary column in the shallow subsurface within sediments deposited on an oxic sea bottom. Dolomite precipitation was temporarily enhanced by an upward flux of methane-rich fluids possibly sourced by gas-hydrate destabilization.

Conversely, from the onset of the MSC onward, calcite (and aragonite) were the dominant authigenic phases. Microbial-orchestrated carbonate precipitation took place just below the sea

639 bottom, covered by chemotrophic microbial mats dominated by giant sulphide-oxidizing bacteria.  
640 The development of these mats was triggered by the establishment of anoxic conditions at the sea  
641 bottom (hampering gypsum deposition), in turn related to density stratification of the water column  
642 and/or enhanced biological productivity in the water column. The high sulphate concentration in the  
643 pore water, related to the presence of concentrated brines and to the physiology of sulphide-  
644 oxidizing bacteria (responsible for the continuous “regeneration” of sulphate) were the main factors  
645 controlling the mineralogical change from dolomite to calcite. These microbialites do not provide  
646 any evidence of sea level lowering at the onset of the MSC as frequently reported, because  
647 sulphide-oxidizing bacteria are not light dependent and can live at any depth. Accordingly, the  
648 contractional features observed in the sediments, that are commonly regarded as a proof of sea level  
649 drop and subaerial exposure, may be ascribed to sediment syneresis due to bacterial EPS  
650 degradation in a subaqueous environment.

651 The results of this study highlight how microbial activity can influence the type of  
652 authigenic products and the resultant fabrics (dolomite beds *versus* microbialites); moreover, they  
653 suggest that care must be taken in the interpretation of the isotope oxygen values in terms of  
654 fluctuating salinity conditions of the water mass, with negative values reflecting dilution events and  
655 positive ones an increase of the rate of the evaporation. The  $^{18}\text{O}$  enrichment of the pre-MSC (early  
656 diagenetic) beds does not necessarily reflect the isotopic composition of sea water but rather the  
657 contribution of diagenetic fluids in the shallow subsurface. In the same way, the sharp shift towards  
658 negative  $\delta^{18}\text{O}$  values at the onset of MSC may reflect complex fractionation processes operated by  
659 sulphate-reducing bacterial communities.

660 Further studies are needed, especially devoted to the characterisation of the biomarker  
661 inventory preserved in the carbonates, that could provide more extensive information on the types  
662 of microbes involved in carbonate precipitation and on the mutual relationships (if any) with  
663 microbes preserved within the gypsum deposited in the shallower part of the Messinian basin(s).  
664 This type of approach can contribute to provide information on the changes of microbial

665 communities at the onset the MSC and on the role played by bacterial activity in modulating  
666 evaporite and carbonate sedimentation during the MSC.

667

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673

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1071 **Figure captions**

1072 **Fig. 1.** A) Structural sketch of NW Italy (modified from Bigi et al., 1990). The asterisk shows the  
1073 location of the Pollenzo section. TH: Torino Hill; MO: Monferrato; AM: Alto Monferrato; BG:  
1074 Borbera-Grue; VVL: Villalevernia-Varzi Line; SVZ: Sestri-Voltaggio zone; IL: Insubric Line. B)  
1075 Regional section in a N-S direction (redrawn after Bertotti and Mosca, 2009; Mosca et al., 2009).  
1076 Location in Fig. 1A.

1077

1078 **Fig. 2.** A) Schematic cross section, flattened at the base of the Pliocene, showing the relationships  
1079 among the Messinian units. PLG: Primary Lower Gypsum unit; RLG: Resedimented Lower  
1080 Gypsum unit; MES: Messinian erosional surface; SKB: Sturani key-bed; CRB: carbonate-rich beds  
1081 (from Dela Pierre et al, 2011). Not to scale. B) Stratigraphic model of the MSC record of Alba  
1082 along a SW-NE cross section flattened at the base of the Pliocene. The location of the Pollenzo  
1083 section is shown. The carbonate-rich beds discussed in the text are marked in yellow (from Dela  
1084 Pierre et al., 2011). Abbreviations as in Fig. 2A. The trace of the cross section is shown in Fig. 1A.  
1085

1086 **Fig. 3.** The Pollenzo section (left) and detail of the upper part of the Sant'Agata Fossili Marls  
1087 (right). ICP data (total carbonates, dolomite and calcite) and stable isotope data of pre-MSC and  
1088 MSC cycles are shown. SKB: Sturani-key bed; RLG: Resedimented Lower Gypsum unit; AAF:  
1089 Argille Azzurre Formation; hb: hemi-ellipsoidal body. Chrono-biostratigraphic data and distribution  
1090 of foraminifers and calcareous nannofossils are from Lozar et al. (2010) and Dela Pierre et al.,  
1091 (2011).

1092

1093 **Fig. 4.** The upper part of the Sant'Agata Fossili Marls at Pollenzo; the carbonate-rich beds  
1094 discussed in the text are shown. From this perspective view bed *a* is not visible. SAF: Sant'Agata  
1095 Fossili Marls; PLG: Primary Lower Gypsum unit.

1096

1097 **Fig. 5.** Pre-MSC beds. A) Outcrop view of bed *a*. Note the sharp lower and upper boundaries. B)  
1098 Polished slab of bed *a*. Burrows (arrows) can be recognised. C) Photomicrograph (plane light) of  
1099 bed *c*; silt-sized terrigenous grains and burrows can be recognised. D) SEM image of a slightly  
1100 etched broken chip of bed *a*. Rhombohedral dolomite crystals are clearly recognisable. E) SEM  
1101 image of a slightly etched broken chip of bed *d*. Pyrite framboids and dolomite crystals are visible.  
1102

1103 **Fig. 6.** MSC beds. A) Outcrop view of the uppermost part of the Sant'Agata Fossili Marls. Beds *e, f*  
1104 and *g* and the hemi-ellipsoidal body (hb) can be recognised. B) Photomicrograph (plane light) of  
1105 bed *e*, showing rounded clasts encircled by circumgranular cracks (arrows). C) Polished slab of bed  
1106 *f*, showing whitish and grey laminae. Some cracks can be recognised within whitish laminae  
1107 (arrows). D) Photomicrograph (plane light) of bed *f*, showing the alternation of carbonate and  
1108 terrigenous-rich laminae. Note the contractional cracks in the carbonate laminae. E)  
1109 Photomicrograph in epifluorescence of bed *f*. Note the stronger fluorescence of the carbonate  
1110 lamina (lower part). Filaments (arrows) can be seen in the carbonate lamina.  
1111

1112 **Fig. 7.** MSC beds. A) Photomicrograph (plane light) of bed *g*. Note the thin lamination and the  
1113 black filaments (arrows) underlined by a concentration of pyrite framboids. B) SEM images of a  
1114 broken chip of bed *f* showing globular calcite crystals with a central hollow. C) Photomicrograph  
1115 (plane light) of bed *g* with a detail of a filament. D) Photomicrograph in epifluorescence of the same  
1116 filament of Fig. 7C. Note its different epifluorescence with respect to the surrounding matrix and  
1117 the abundant pyrite framboids preserved within it.  
1118

1119 **Fig. 8.** The hemi-ellipsoidal body. A) Outcrop view. B) Polished slab of a sample collected in the  
1120 upper part of the body; note the wrinkled lamination. C) and D) Photomicrographs in plane light  
1121 and in epifluorescence of some filaments. Note in D) the stronger epifluorescence of the calcite  
1122 infilling of a large filament. E) Photomicrograph (plane light) of curved filaments surrounded by

1123 fringing aragonite (arrows). The central portion of the intergranular voids is filled with calcite (cc).  
1124 F) SEM image of a slightly etched broken chip showing slightly curved calcite filaments,  
1125 surrounded by aragonite fringes (ar).

1126

1127 **Fig. 9.** The hemi-ellipsoidal body: pyrite framboids growing on aragonite fringes.

1128

1129 **Fig. 10.** Genesis of the pre-MSC carbonate-rich beds at the sulphate-methane interface (SMI).

1130 A) During formation of beds *a* and *b*, bacterial sulphate reduction was coupled to anaerobic  
1131 oxidation of methane (AOM); methane derived (at least in part) from gas hydrate (GH)  
1132 destabilization. B) Dolomite precipitation in beds *c* and *d* was induced by bacterial sulphate  
1133 reduction alone, fuelled by organic matter oxidation. In these beds the dolomite content is lower  
1134 than in beds *a* and *b*. Depth of the SMI below the sea floor was probably of few metres and was  
1135 shallower for beds *a* and *b*, due to the larger supply of methane from below.

1136

1137 **Fig. 11.** Genesis of the MSC carbonate-rich-beds. Carbonate precipitation was triggered by  
1138 bacterial sulphate reduction in organic-matter-rich anoxic sediments immediately below the sea  
1139 floor; the latter was covered by filamentous sulphide-oxidizing bacteria (F). Since sulphate was not  
1140 completely consumed, calcite was favoured. Dolomite could precipitate only later at the sulphate-  
1141 methane-interface (SMI). For further detail see text.

1142

1143 **Fig. 12.** Formation of laminated carbonate beds.

1144 A) A mat of filamentous sulphide-oxidizing bacteria developed at the sea floor, sustained by a  
1145 sulphide flux sourced by bacterial sulphate reduction working in the shallow subsurface; here active  
1146 calcite precipitation took place. B) A layer of organic-matter-poor terrigenous sediment buried the  
1147 chemotrophic mat, slowing down the activity of sulphate-reducing bacteria. C) After the terrigenous  
1148 influx ceased, the activity of sulphate-reducing bacteria resumed, focused in organic-rich layers (a

1149 buried chemotrophic mat in this example). The ensuing calcite (and pyrite) precipitation preserved  
1150 the dead bacterial filaments, while a new chemotrophic mat developed on the aggraded sea floor.  
1151 Calcite was followed by dolomite precipitation (see Fig. 11). For further detail, see text.

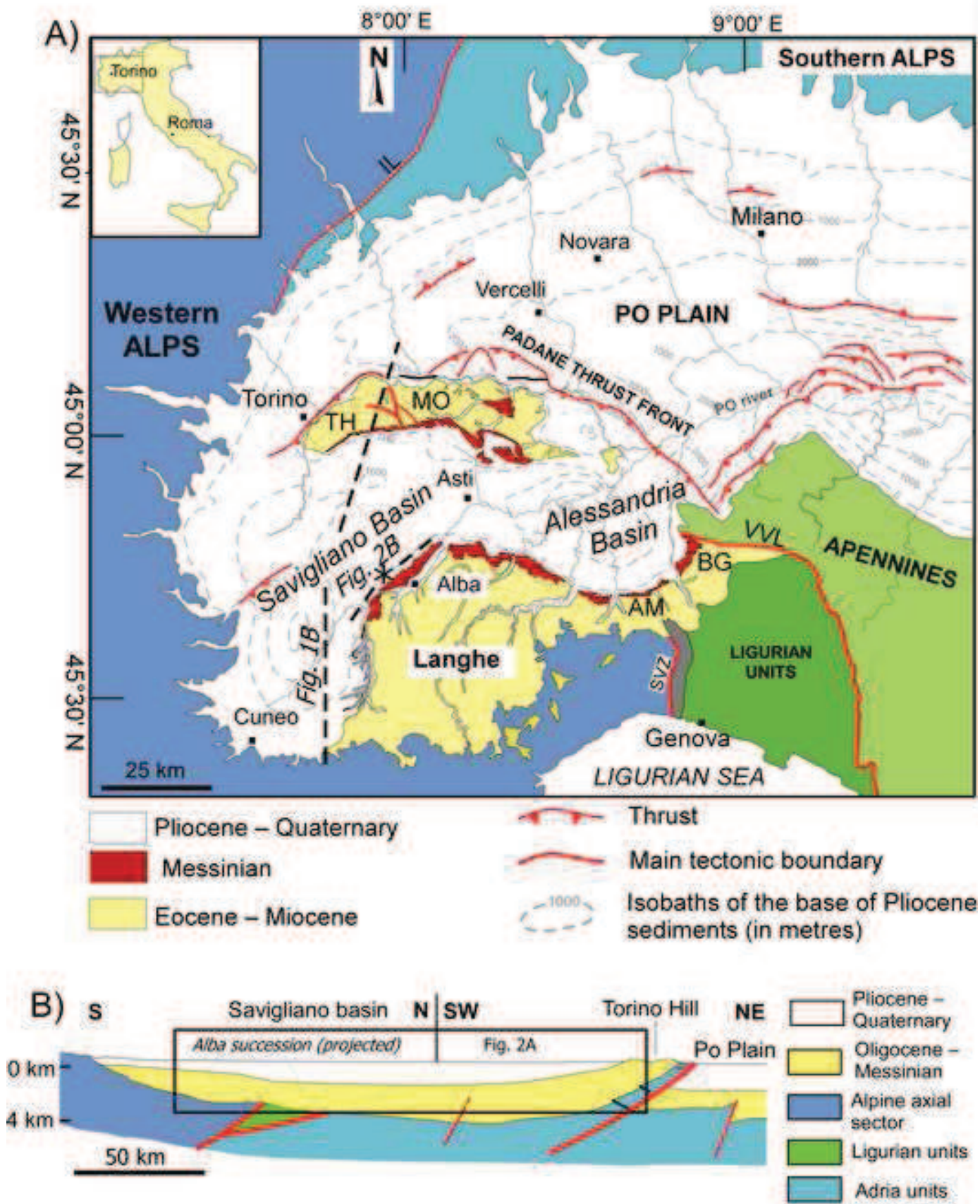
1152  
1153 **Table 1.** ICP data of pre-MSC (light grey shadow) and MSC (dark grey shadow) sediments; h.m:  
1154 homogeneous marl; l.s.: laminated shale; T.C: total carbonate.

1155  
1156 **Table 2.** Percentage of dolomite and calcite with respect to the total carbonate (T.C.) content in the  
1157 pre-MSC (light grey shadow) and MSC (dark grey shadow) carbonate-rich beds.

1158  
1159 **Table 3.** Stable isotope data of pre-MSC (light grey shadow) and MSC (dark grey shadow)  
1160 sediments. Carbonate-rich beds are in bold. Hem. body: hemi-ellipsoidal body.

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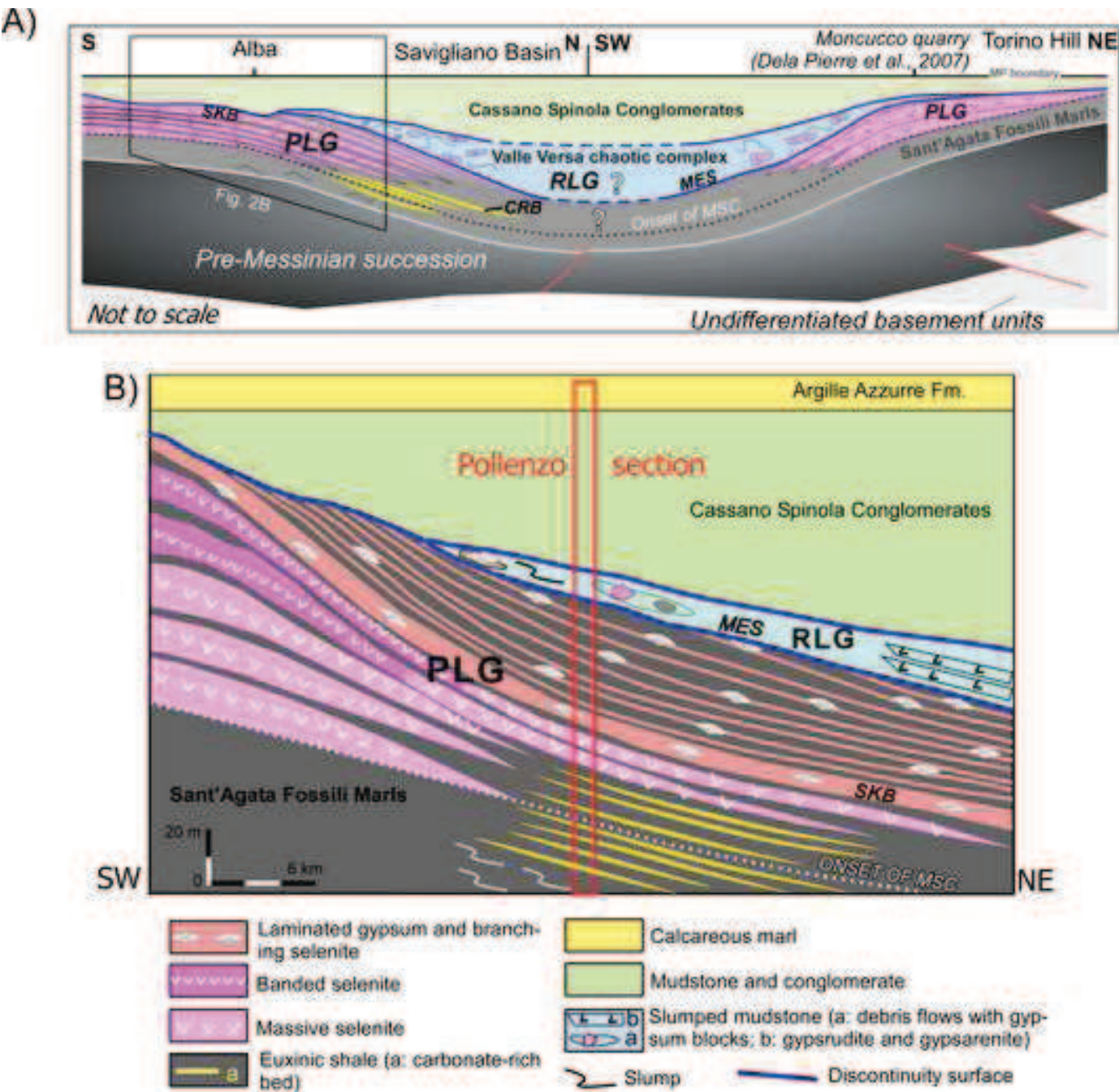
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Dela Pierre et al. Fig. 1

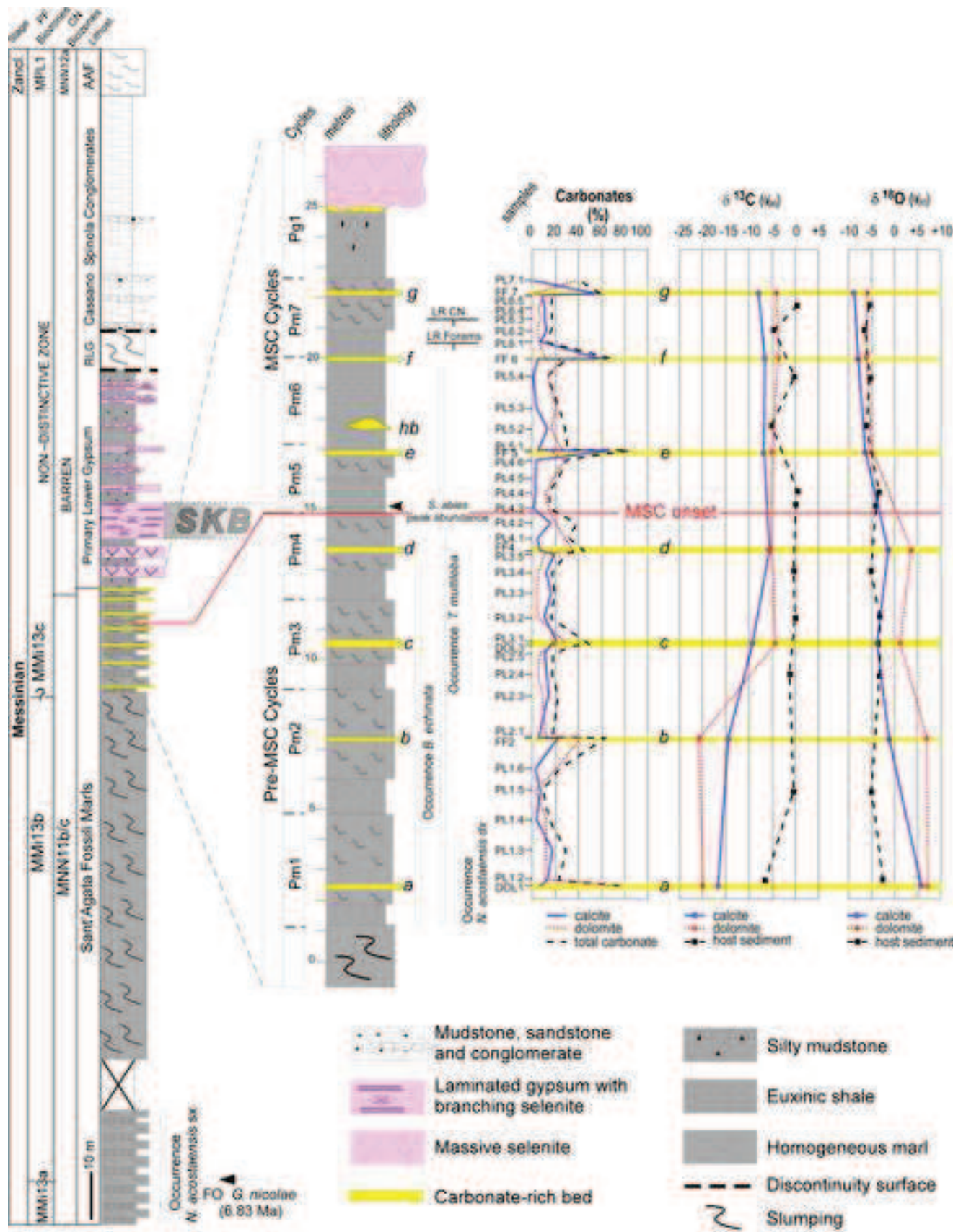


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Dela Pierre et al. Fig. 2

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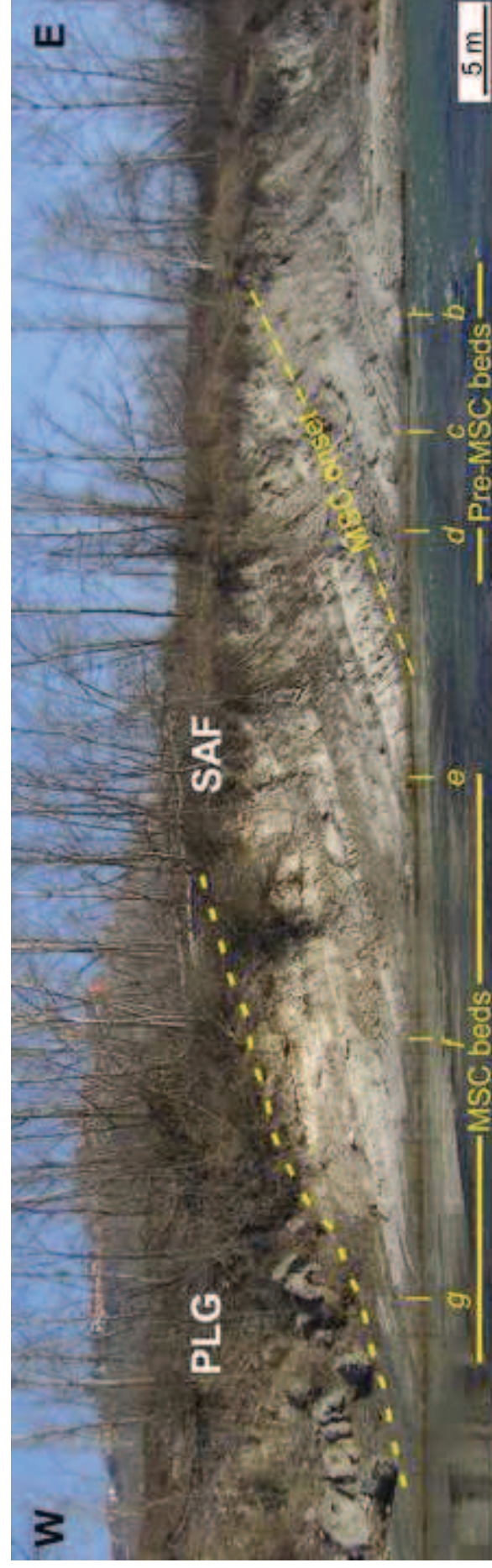


Dela Pierre et al., Fig. 3



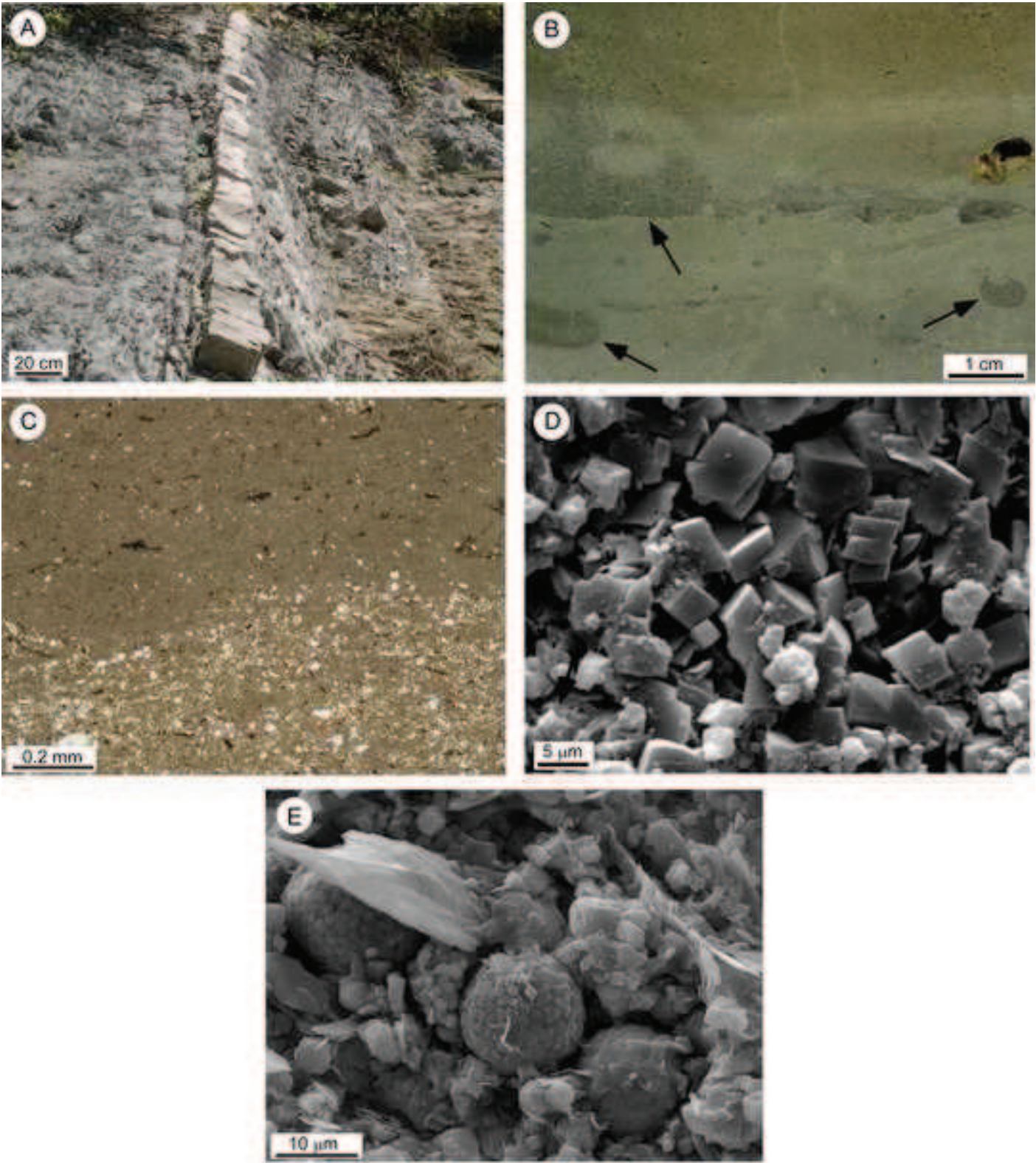
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Dela Pierre et al. Fig. 4

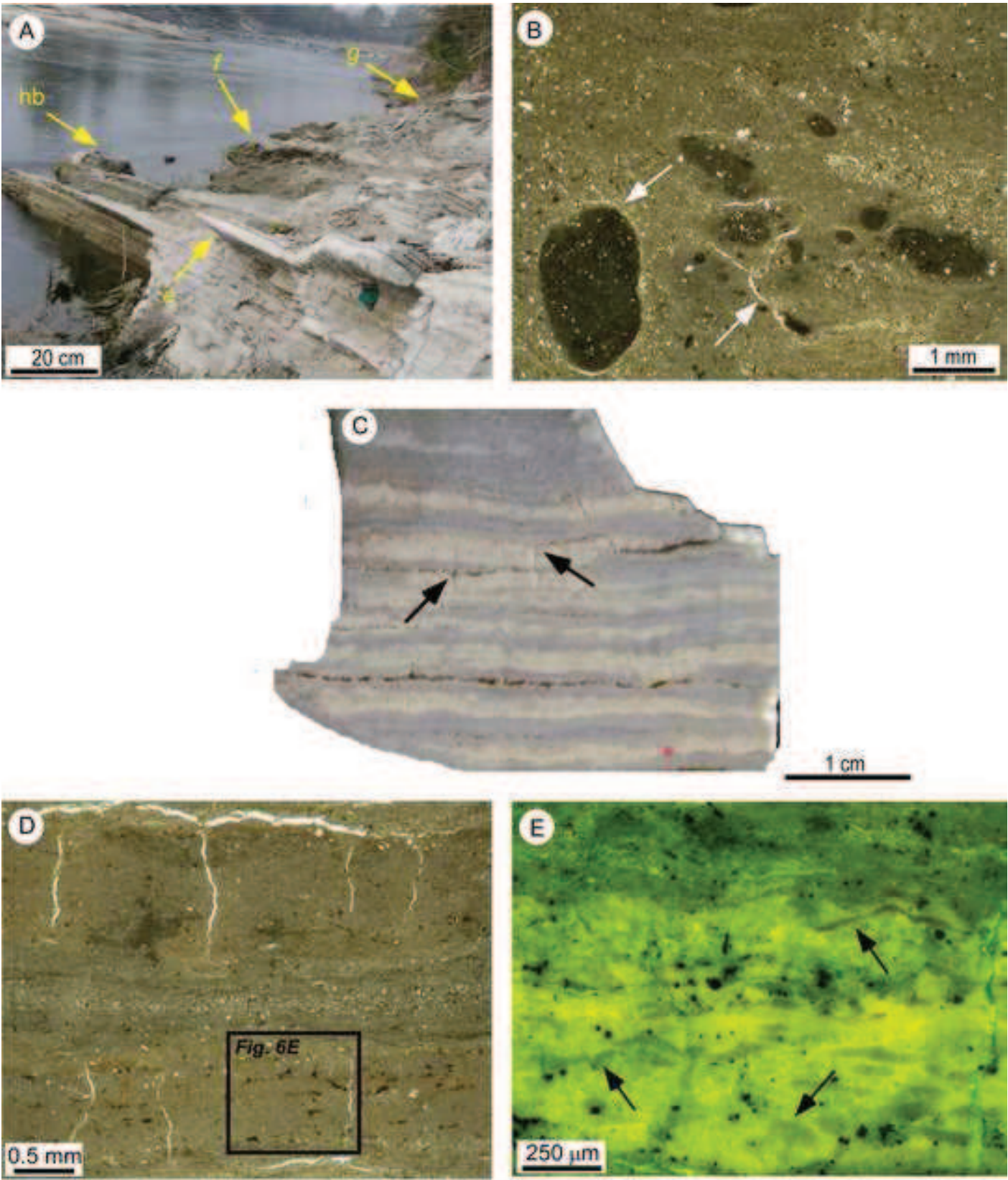
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Dela Pierre et al., Fig. 5

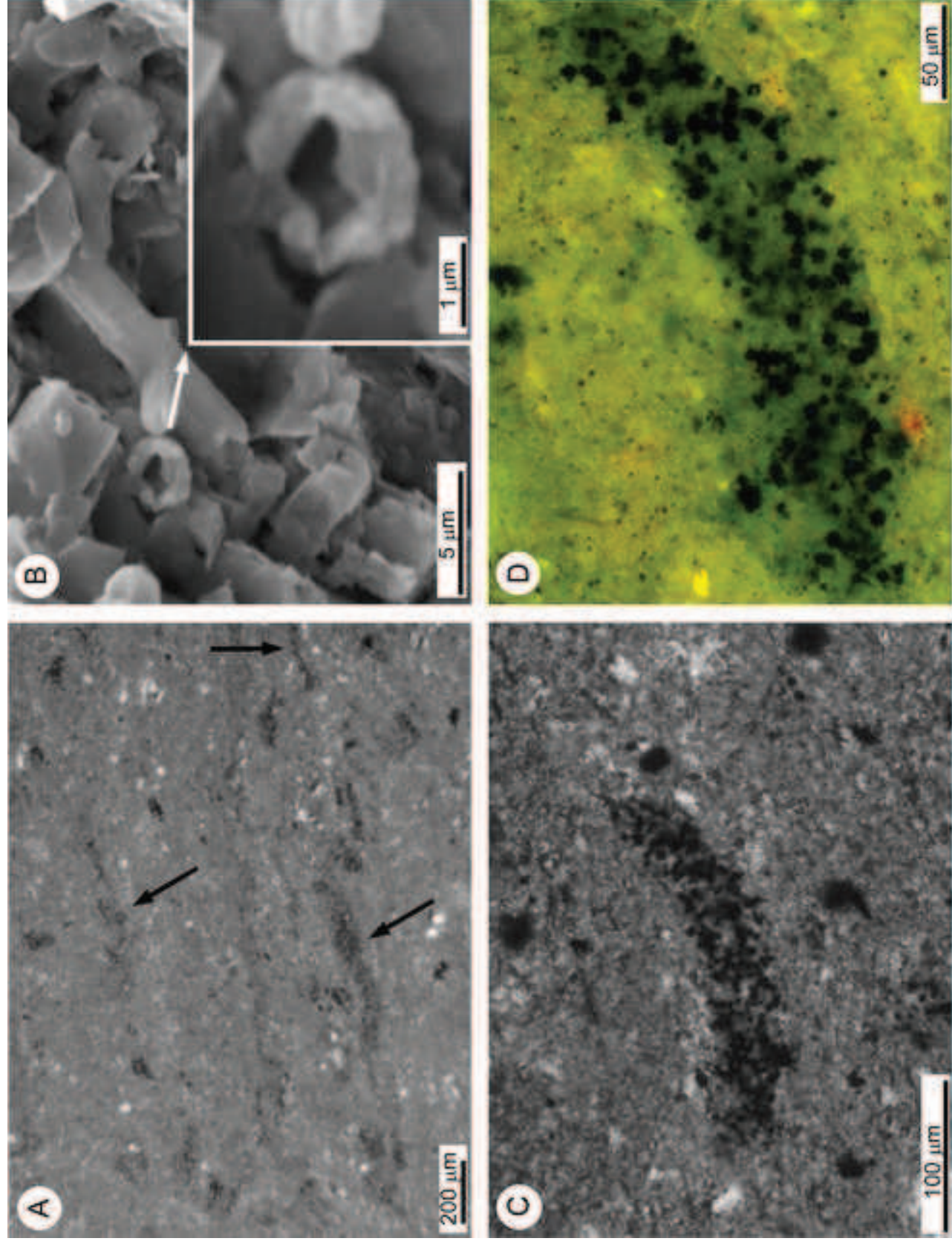


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Dela Pierre et al. Fig. 6

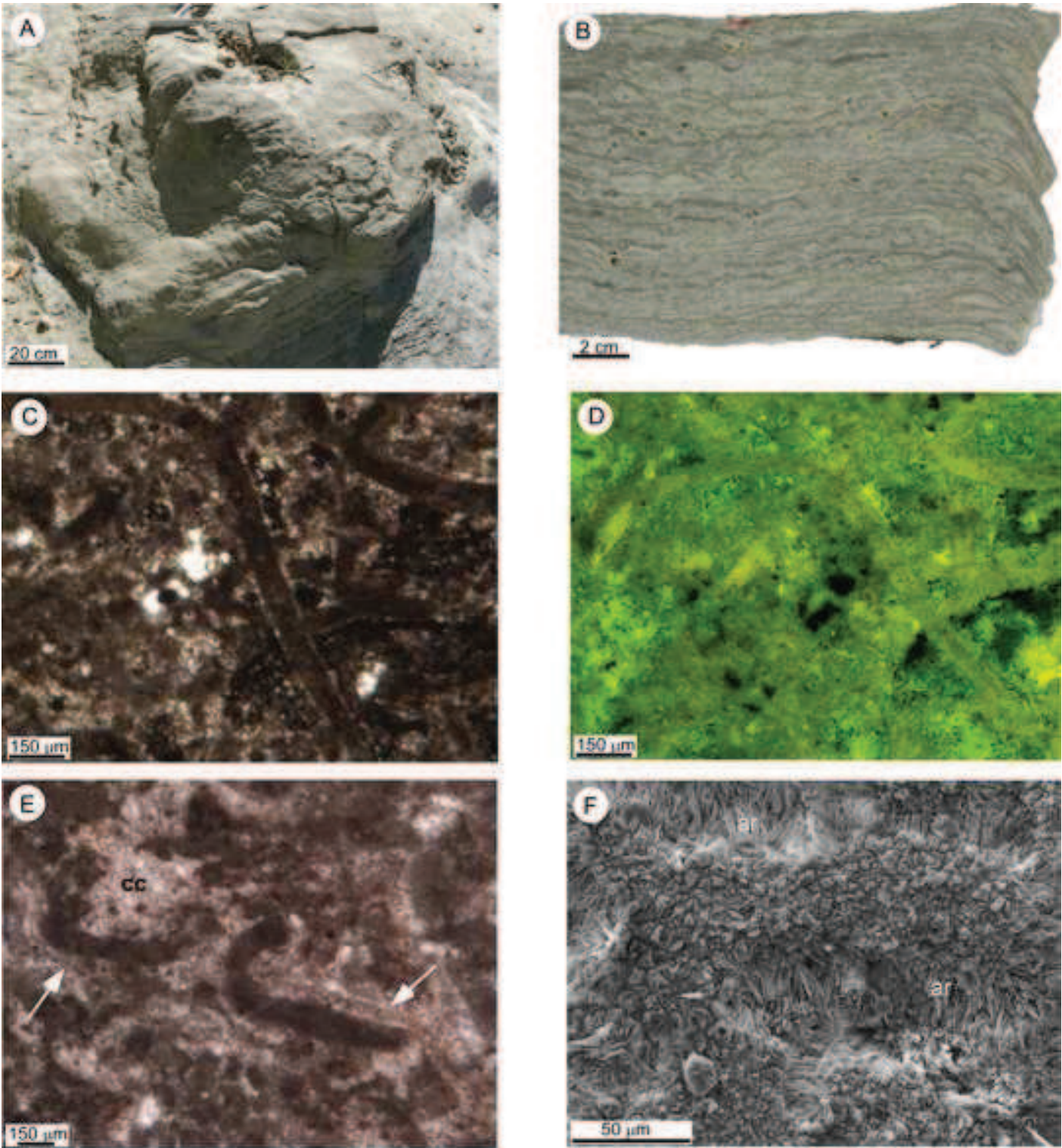




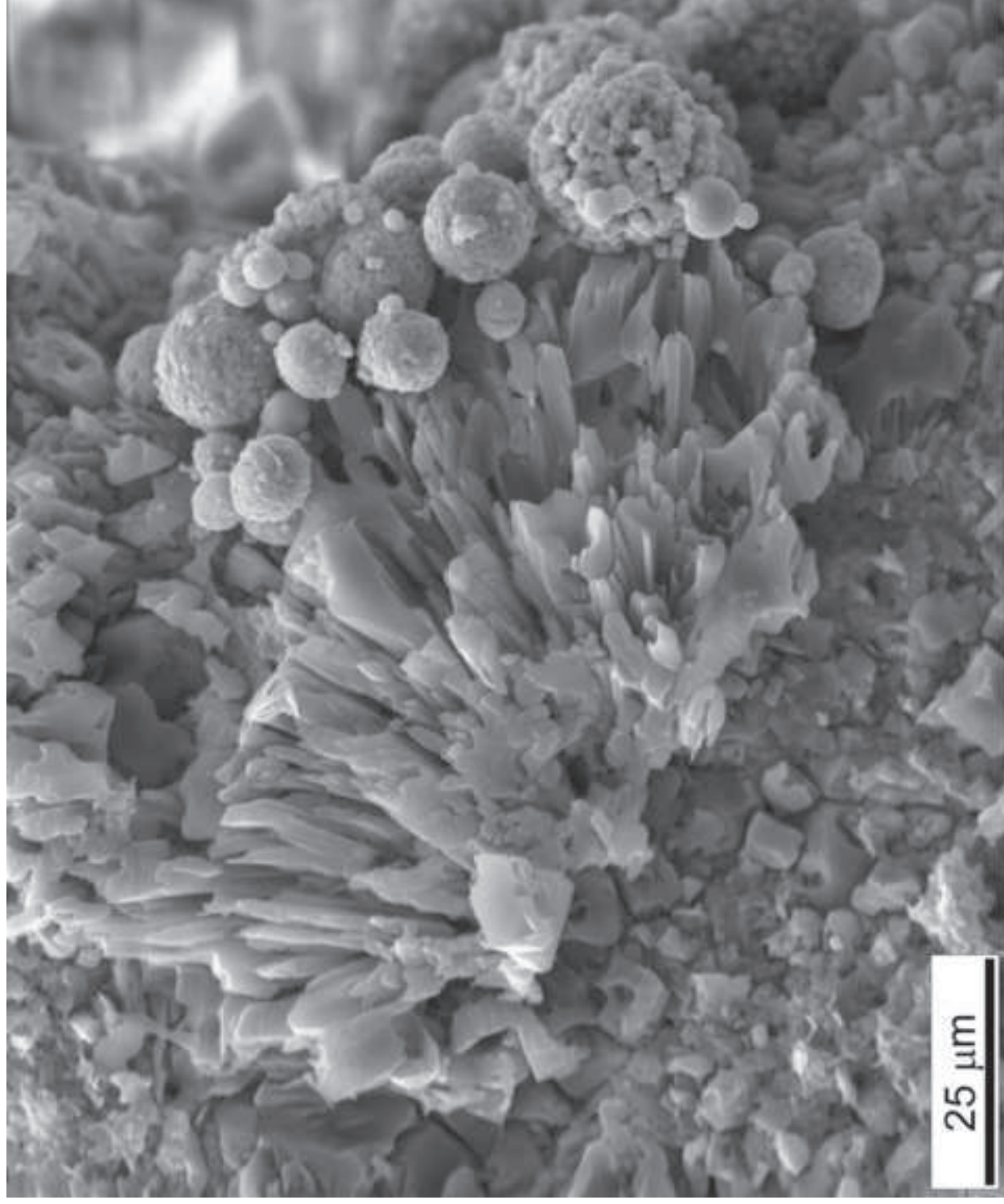
Dela Pierre et al. Fig. 7



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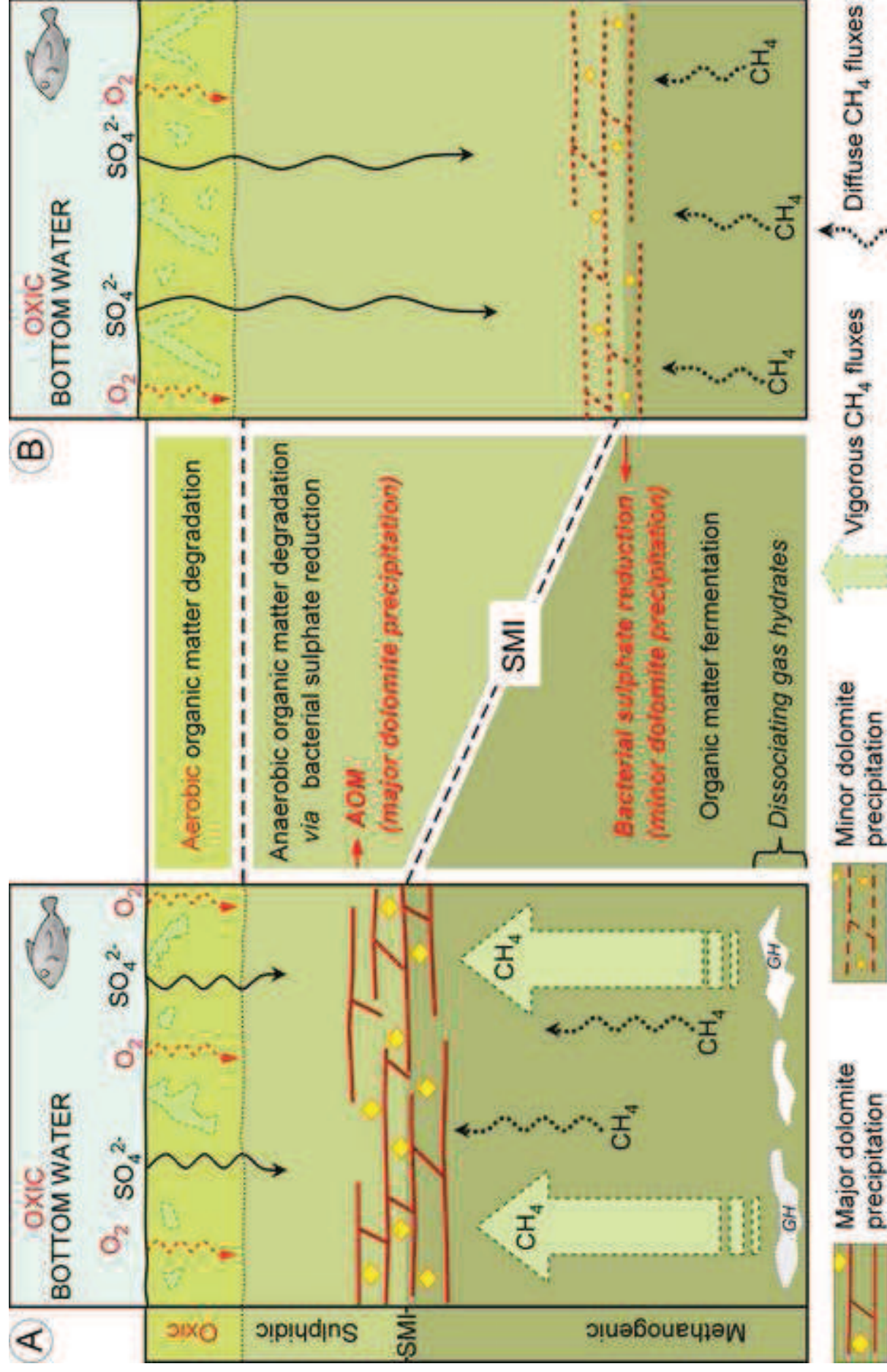


Dela Pierre et al. Fig. 8

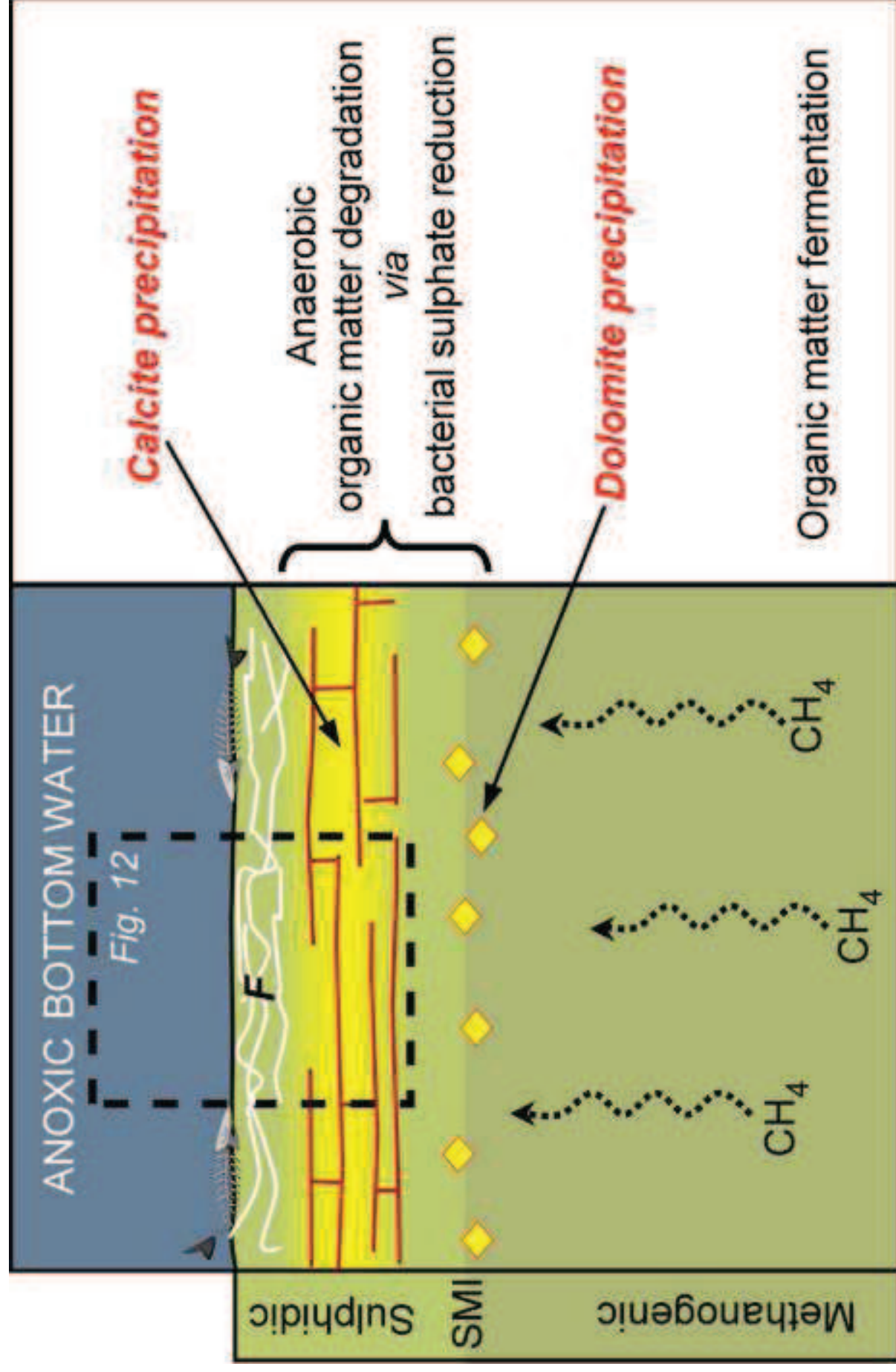


Dela Pierre et al. Fig. 9



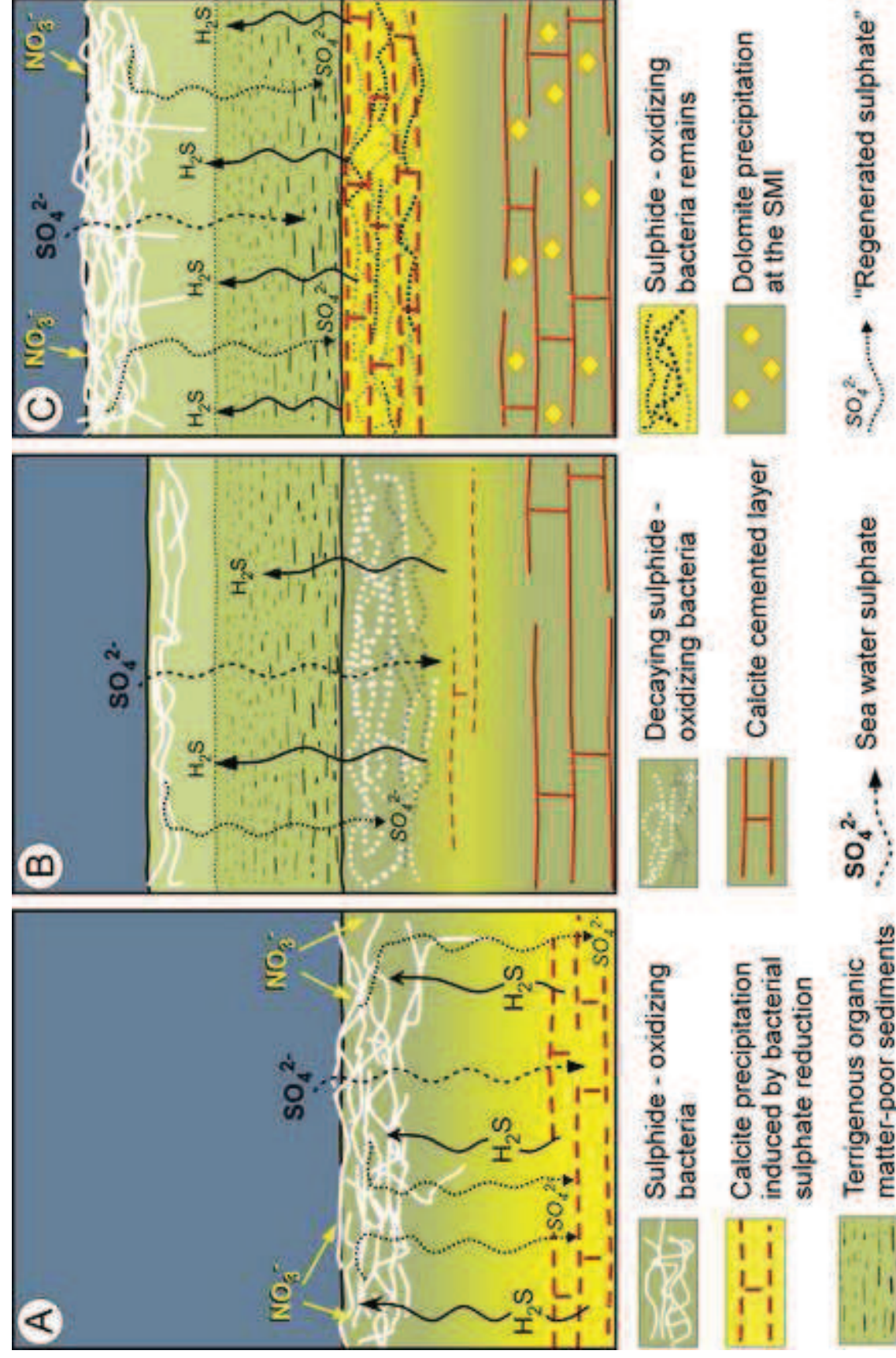


Dela Pierre et al., Fig. 10



Dela Pierre et al., Fig. 11





<i>Sample</i>		<i>Cycle</i>	<i>T.C.</i> [% on the whole rock]	<i>Dolomite</i> [% on the whole rock]	<i>Calcite</i> [% on the whole rock]
PL7.1	(h.m.)	Pm7	40.7	39.4	1.3
<b>FF7</b>	<b>(bed g)</b>	<b>Pm7</b>	<b>59.0</b>	<b>3.1</b>	<b>55.9</b>
PL6.5	(l.s.)	Pm7	17.2	9.1	8.0
PL6.4	(l.s.)	Pm7	16.7	5.8	10.9
PL6.3	(l.s.)	Pm7	16.7	6.1	10.6
PL6.2	(l.s.)	Pm7	16.4	4.3	12.2
PL6.1	(l.s.)	Pm7	13.2	5.8	7.4
<b>FF6</b>	<b>(bed f)</b>	<b>Pm6</b>	<b>69.1</b>	<b>11.0</b>	<b>58.1</b>
PL 5.4	(l.s.)	Pm6	13.6	12.8	0.7
PL 5.3	(l.s.)	Pm6	23.4	20.1	3.3
PL 5.2	(l.s.)	Pm6	24.9	14.1	10.8
PL 5.1	(l.s.)	Pm5	30.7	25.4	5.2
<b>FF5</b>	<b>(bed e)</b>	<b>Pm5</b>	<b>84.6</b>	<b>16.7</b>	<b>67.9</b>
PL 4.6	(h.m.)	Pm5	30.3	27.1	3.2
PL 4.5	(l.s.)	Pm5	22.4	19.4	3.0
PL 4.4	(l.s.)	Pm5	16.1	13.3	2.8
PL 4.3	(l.s.)	Pm5	17.0	15.5	1.5
PL 4.2	(h.m.)	Pm4	39.1	18.3	20.8
PL 4.1	(h.m.)	Pm4	33.9	29.7	4.2
<b>FF4</b>	<b>(bed d)</b>	<b>Pm4</b>	<b>45.1</b>	<b>37.5</b>	<b>7.6</b>
PL3.5	(h.m.)	Pm4	31.6	12.3	19.3
PL3.4	(l.s.)	Pm4	17.2	5.1	12.1
PL3.3	(l.s.)	Pm4	20.4	4.2	16.3
PL3.2	(h.m.)	Pm3	15.7	5.0	10.7
<b>PL3.1</b>	<b>(bed c)</b>	<b>Pm3</b>	<b>48.2</b>	<b>24.9</b>	<b>23.3</b>
<b>DOL3</b>	<b>(bed c)</b>	<b>Pm3</b>	<b>36.1</b>	<b>20.3</b>	<b>15.9</b>
PL2.5	(h.m.)	Pm3	18.2	7.0	11.2
PL2.4	(l.s.)	Pm3	17.5	4.8	12.8
PL2.3	(h.m.)	Pm2	22.4	8.3	14.1
PL2.1	(h.m.)	Pm2	17.9	12.2	5.7
<b>FF2</b>	<b>(bed b)</b>	<b>Pm2</b>	<b>63.1</b>	<b>42.9</b>	<b>20.2</b>
PL1.6	(h.m.)	Pm2	23.0	20.5	2.5
PL1.5	(l.s.)	Pm2	9.7	2.6	7.2
PL1.4	(h.m.)	Pm2	15.1	11.7	3.5
PL1.3	(h.m.)	Pm1	29.6	12.1	17.5
PL1.2	(h.m.)	Pm1	23.5	10.4	13.1
<b>DOL1</b>	<b>(bed a)</b>	<b>Pm1</b>	<b>76.1</b>	<b>69.9</b>	<b>6.2</b>

Dela Pierre et al. Tab. 1

<i>Sample</i>		<i>Cycle</i>	<i>Dolomite</i> [% vs T.C.]	<i>Calcite</i> [% vs T.C.]
FF7	(bed g)	Pm7	5.2	94.8
FF6	(bed f)	Pm6	15.9	84.1
FF5	(bed e)	Pm5	19.8	80.2
FF4	(bed d)	Pm4	83.3	16.7
PL3.1	(bed c)	Pm3	51.7	48.3
DOL3	(bed c)	Pm3	56.0	44.0
FF2	(bed b)	Pm2	68.0	32.0
DOL1	(bed a)	Pm1	91.9	8.1

Dela Pierre et al., Tab. 2

<i>Sample</i>	<i>Cycle</i>	$\delta^{13}C_{cal}$ [‰]	$\delta^{18}O_{cal}$ [‰]	$\delta^{13}C_{dol}$ [‰]	$\delta^{18}O_{dol}$ [‰]
STR 8 (hem. body)	Pm6	-9.2	-7.2		
STR 7 (hem. body)	Pm6	-8.7	-6.9		
STR 4 (hem. body)	Pm6	-8.2	-7.7		
<b>FF 7 (bed g)</b>	<b>Pm7</b>	<b>-7.9</b>	<b>-8.8</b>	<b>-4.0</b>	<b>-5.8</b>
PL 6.4	Pm7	+0.5	-5.4		
PL 6.2	Pm7	-4.7	-6.4		
<b>FF 6 (bed f)</b>	<b>Pm6</b>	<b>-6.8</b>	<b>-7.9</b>	<b>-3.9</b>	<b>-6.1</b>
STR 8 (hem. body)	Pm6	-9.2	-7.2		
STR 7 (hem. body)	Pm6	-8.7	-6.9		
STR 4 (hem. body)	Pm6	-8.2	-7.7		
PL 5.4	Pm6	-0.4	-5.2		
PL 5.2	Pm6	-5.0	-6.0		
<b>FF 5 (bed e)</b>	<b>Pm5</b>	<b>-6.7</b>	<b>-6.5</b>	<b>-5.0</b>	<b>-4.9</b>
PL 4.4	Pm5	+0.3	-3.4		
PL 4.3	Pm5	0.0	-4.1		
<b>FF 4 (bed d)</b>	<b>Pm4</b>	<b>-5.7</b>	<b>-1.2</b>	<b>-5.2</b>	<b>+3.6</b>
PL 3.4	Pm4	+0.5	-5.1		
PL 3.2	Pm3	0.0	-3.3		
<b>FF 3 (bed c)</b>	<b>Pm3</b>	<b>-9.2</b>	<b>-3.9</b>	<b>-4.4</b>	<b>+1.3</b>
PL 2.4	Pm3	-1.0	-3.2		
<b>FF 2 (bed b)</b>	<b>Pm2</b>	<b>-14.5</b>	<b>-1.0</b>	<b>-21.0</b>	<b>+6.9</b>
PL 1.5	Pm2	-0.6	-5.1		
PL 1 .2	Pm1	-6.5	-2.5		
<b>FF 1 (bed a)</b>	<b>Pm1</b>	<b>-16.7</b>	<b>+5.7</b>	<b>-19.8</b>	<b>+7.0</b>

Dela Pierre et al., Tab. 3